REACTIONS OF COPPER AND CADMIUM IN SOILS.

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'To travel hopefully is a better thing than to arrive, and the true success is to labour'.

Robert Louis Stevenson (1850-1894).
Virginibus Puerisque - 'El Dorado'.

Table of Contents.

SUMMARY.

This project examines some of the factors influencing the interactions of the metals copper and cadmium with a range of soils from the United Kingdom, at levels which may be said to mimic low level contamination.

Applying the traditional batch technique, in alliance with AAS (Atomic Absorption Spectrophotometry) and ISE's (Ion Selective Electrodes), the physical and chemical parameters of the soils which influence the removal of these metals from incident solutions, as well as the effect the solution chemistry has upon the process, was examined.

No clear relationship could be found between the 'classical' soil properties and the retention of either metal, although pH did seem to play a role in solution Cu chemistry, and the presence of carbonates in soils greatly increased their ability to remove Cd from solution. The relationship between pH and organic matter in solution can be crucial in considerations of solution chemistry.

The presence of other polyvalent cations had a minimal influence upon the uptake characteristics for either metal, leading to the conclusion that groups of discrete, high affinity, sites exist, over and above the CEC (Cation Exchange Capacity), for Cu and Cd at up to 2.5μM Cu or Cd/g of soil.

Anions, in terms of the type and their concentration had a variable influence upon Cu and Cd soil-solution interactions. An organic ligand such as Citrate acts much as expected, complexing and maintaining metal levels (total) in solution. Inorganic complexation, by NO_3^-, Cl^- and SO_4^{2-} has a smaller influence, although chloride is expected to, and does sequester Cd to the solution phase - sulphate

-Cd complexation is anomalous in this respect, implying that the $(CdSO_4)^o$ species may be being sorbed. Cu uptake follows a pattern which is inversely related to the influence each anion has on the pH of the system. Changing the ionic strength (I) of the systems has a predictable influence on Cd uptake; as I increases, $[Cd]_{sorbed}$ decreases ie. not all of the differences in the results described above can be due solely to the type of anion. In this instance, ΔI has little influence on Cu uptake, suggesting that the formation of Nitrate complexes is not a limiting factor with regard to soil uptake, and that more stable species control its destiny.

Sorption kinetics suggest that the free ion levels stabilize within minutes of the solution coming into contact with the soil, although longer term studies suggest that there is a prolonged change in the activity, but on a far less dramatic scale than in the initial minutes of the reaction. In the short term, uptake may be followed by a release of the free metal ion - possibly due to a pH feedback mechanism.

Data summation could be achieved for Cd via the logarithmic van Bemmelen-Freundlich relationship, whilst for Cu no mathematical relationship could be found which resulted in a single, easily rationalized, straight line - a two-constant version of the above equation is the simplest to use.

Chapter 1. Introduction.

1.1. Environmental and Biochemical Aspects of Cadmium and Copper.

In geochemical terms, any elements which occur at levels below approximately 0.1% of the lithosphere may be categorized as "trace elements", and into this category fall the transition elements Cu and Cd (Davies 1980).

Cu is present in rocks at approximately 70 mg/kg, whilst in soil this figure can range from 2 - 100 mg/kg.

Cd occurs at very much lower concentrations: 0.2 mg/kg for rocks and 0.01 - 0.70 mg/kg in soils (Lindsay 1979; Archer & Hodgson 1987).

However, whilst the presence of copper in the environment is generally to be viewed as desirable, that of cadmium is not.

Copper plays an important role in many plant and animal biochemical and physiological actions (Phipps 1976; Lonergan *et al* 1981; M^{c}Donald *et al* 1981; Wild 1988) as a redox site and also as a steric influence in many proteins. Although its role as a required nutrient for plants and animals is definite, copper is a "micro" nutrient ie. one which is required only in small amounts, indeed, at high levels, copper is positively toxic (MAFF 1980) to both animals and plants.

A role in the life cycle of either plants or animals has not been demonstrated for cadmium, its presence in soils has been shown to depress crop yields (MAFF 1980), whilst MacNicoll and Beckett (1985) have stated that yield reduction will probably occur if the tissue content of any crop exceeds 5 mg/kg Cd (and 10 mg/kg for Cu). Some crops demonstrate, however, a remarkable ability to accumulate

high levels of Cd without showing any phytotoxicity (Bingham 1979; Adam *et al* 1989) which must pose a problem to any consumer.

Cadmium has a well-documented toxicology in mammals (Phipps, 1976; Stoeppler & Piscator 1988); it tends to accumulate in the liver (bound to the protein, Metallothionein) causing chronic tissue damage and, ultimately, hypertension. Cadmium can displace other metals from within proteo-enzyme structures, resulting in their failure (possibly replacing zinc and calcium (Mortvedt *et al* 1972; Phipps 1976)). Table 1.1. lists some enzymes which rely upon the presence of a transition metal ion for their activity, whilst table 1.2. outlines some of the principal mineral sources of copper and cadmium.

Table 1.1. Metal Containing Enzymes.

Copper-containing enzymes
- Ascorbic Acid Oxidase
- Cytochrome Oxidase
- Tyrosinases
- Haemocyanin

Zinc-containing enzymes
- Carbonic Anhydrases
- Carboxypeptidases
- Dehydrogenases
- Alkaline Phosphatases

(Cotton & Wilkinson 1972; Phipps 1976)

Table 1.2. The Principal,non-anthropogenic, sources of Cu and Cd.

Copper;	Chalcopyrite	$CuFeS_2$
	Malaelnite	$Cu_2(HO)_2CO_3$
	Azurite	$Cu_3(HO)_2(CO_3)_2$
Cadmium	Sphaelerite	Zn/CdS
	Smithsonite	$Zn/CdCO_3$

Cadmium is frequently found in association with zinc minerals, given that Cd and Zn have such different ionic radii, this would appear to be quite an unusual phenomena: Zn 83 pm and Cd 103 pm (Emsley 1989).

The figures quoted at the beginning of this chapter give some indication of the normal soil content of copper and cadmium, however, there are bound to be anomalies, and these can be split into two categories:

1. Geological concentrations of ores/metal bearing rocks
2. Man-made ie. pollution

Webb *et al* (1978) and Webb and Thornton (1980) provide an excellent survey of the distribution of trace elements in England and Wales, pinpointing areas of high native copper and cadmium (an up to date survey of this type for Scotland is, sadly, lacking). The compilation of "The Wolfson Geochemical Atlas of England and Wales" (Webb *et al* 1978) led to a more intensive study of one area in particular; the Shipham report (Thornton 1988) was the result of research prompted by the discovery that the soil around the village of Shipham contained as much as 800 mg/kg Cd.

The Shipham report (Thornton 1988) really straddles the two categories listed above in that the high native levels of cadmium do exist in the geological composition of this location, but the activity of mining (for lead) produced vast amounts of waste materials, and these were transported via

rain water run-off to soils where they were retained (Dudley *et al* 1988).

A major source of trace element input to agrarian systems is the use of animal slurries (pig slurry being particularly rich in copper), municipal and industrial sewage and sludge as sources of nitrogen, phosphorus, potassium and organic matter (Cooke 1982).

The amount of these materials being produced is increasing, and land disposal is being more frequently used as a means of dealing with them (Lake *et al* 1984) (particularly in the light of the "London agreement" of 1988 (Kasoulides 1988) which prohibits sea dumping of these waste materials). The metal contents of sludges etc. are quite variable (see table 1.3.).

Table 1.3. Total Cu and Cd levels (mg/kg) in some waste materials.

	SEWAGE SLUDGE[1]		REFUSE COMPOST[2]		ACTIVATED SLUDGE[2]	
	Cu	Cd	Cu	Cd	Cu	Cd
ENGLAND & WALES	800	12	511	14.3	473	18.3
SWEDEN	560	67				

(1.MAFF 1980; 2. Chu & Wong 1988)

Jarvis and Jones (1980) pointed out, though, that at a rate of application of 100 $t.ha^{-1}$, a material containing 7g $Cd.t^{-1}$, will add approximately 0.3g $Cd.t^{-1}$ to the soil (at a depth of 15cm) - this is still not a very great amount, but it does represent quite an addition to the native levels.

Waste materials from power stations can be employed in reclamation schemes as a mineral amendment. Even if used

as a landfill material, the possibility of contamination via run-off cannot be discounted. Table 1.4. gives some examples of the levels of Cu and Cd found in some power generation waste products.

Table 1.4. Total Cu and Cd levels (mg/kg) in some power generation waste materials

	US FLY ASH[1]	FGD WASTE[2]	DANISH FLY ASH[2]
Cu	45 - 616	16	47
Cd	0.1 - 3.8	0.43	0.06

(FGD = Flue Gas Desulphurization)

(1. MAFF 1980; 2. Nielsen & Bertelsen 1988)

The particulate output from smelters and power stations has also been noted as a significant contributor to the levels of trace elements in soils in their immediate environment (Davies 1980; Kuo *et al* 1983). The emissions from a coal fired power station can be as high as 65 kg. Cd yr^{-1} and 473 kg. Cu yr^{-1} (MAFF 1980). This, combined with other impurities, leads to a typical wet and dry deposition of < 10g Cd $ha^{-1}.yr^{-1}$ and 10 - 500 g. Cu $ha^{-1}.\ yr^{-1}$ (MAFF 1980).

Some further sources of Cu and Cd are listed below in table 1.5. (source; Bolt and Bruggenwert, 1978)

Table 1.5. Common Anthropogenic Sources of Cd and Cu.

Cu: Brass, alloys, tubing, fungicides, pig and poultry feed additives

Cd: Paints, plastics, batteries, fungicides, oil, car tyres[1], phosphatic fertilizers[2].

([1]- Zn compounds are used in the process of vulcanization; [2] -superphosphate; 50 mg/kg (Williams & David, 1973))

1.2. The Chemistry of Copper and Cadmium.

(unless otherwise stated, data and information in this section are from Cotton & Wilkinson (1972, 1976)).

1.2.1. Copper.

Copper has the atomic number 29, is in the first row of transition elements (group IB) and has the electronic structure:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

The positioning of the $4s^1$ electron is such that it is poorly shielded from the nucleus of the atom. S orbitals can penetrate underlying d orbitals- thus the effective nuclear charge which the s electron is subjected to is relatively high and, hence, the first ionization potential of Cu is greater than would have been predicted from observations of the first ionization potentials of other elements in the same period (Douglas *et al* 1983).

The presence of a single valence electron might suggest a similarity between copper and the group I metals, but this is not the case. Neither does Cu behave in a similar fashion to its group partners Ag and Au.

Despite the positive charge which exists on copper in its first ionized state, the removal of a second electron can, and does, proceed relatively easily, and the divalent Cu (II) ion is the most recognized and stable of the ionic forms of copper. Table 1.6. lists the ionization potentials of copper - its period analogue, K, is included for the sake of comparison.

Table 1.6. Ionization Potentials of Cu, Group 1B and a Group I Metal

$Cu^0 \longrightarrow Cu^+$ E = 745.4 kJ.mol^{-1}

$Cu^+ \longrightarrow Cu^{2+}$ E = 1958 kJ.mol^{-1}

$K^o \longrightarrow K^+$ E = 419.0 kJ.mol^{-1}

(Emsley 1989)

The monovalent form of copper is stable only at concentrations below 10^{-2}M and in non-aqueous media (Burgess 1978). In the absence of reducing conditions and stabilizing ligands (as in redox enzymes), a disproportionating reaction spontaneously occurs, greatly diminishing the amount of Cu (I) present in solution (Phipps 1976).

$$2Cu^+_{(aq)} \quad Cu^0_{(c)} + Cu^{2+}_{(aq)} \quad K = 10^6$$

$$\Delta G^0 = -35.6 \text{ kJ.mol}^{-1}$$

The Cu(II) ion forms highly stable complexes with multi-dentate ligands, especially coordinating with N and O atoms. In aqueous solution, the free Cu(II) ion may be described as $[Cu(H_2O)_6]^{2+}$, although, due to ligand field effects (The Jahn-Teller phenomenon) two of the water molecules will not be bound to Cu(II) as tightly as the other four. Additionally, depending upon the pH and copper concentration, polynuclear complexes may form in solution (Burgess 1978). $Cu_2(HO)_3^+$, $Cu_2(HO)_2^{2+}$, $Cu_3(HO)_2^{4+}$, $Cu_3(HO)_4^{2+}$ and $Cu_2(HO)_2^+$ have all been proposed as solution forms of Cu (II).

1.2.2. Cadmium.

Cadmium has the atomic number 48, is in the second row of transition elements (Group IIB) and has the following electronic configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$$

The univalent form of cadmium is found only in molten or fused salts, hence our concern is only with the divalent form. As Cd (II) has a filled d-shell, there is no ligand field stabilization as found in Cu (II).

Cd and Zn (a Group IIb partner) share very similar chemistries, and in the solid phase, both favour tetrahedral crystal environments (Zincblende and Wurzite), which may explain the high incidence of Cd association with zinc in minerals.

The principle aqueous form of Cd is the Hexaquo ion $[Cd(H_2O)_6]^{2+}$, but at high concentrations $[Cd_2(HO)]^{3+}$ and $[Cd_4(HO)_4]^{4+}$ have been observed.

The ligands favoured by Cd for complexation tend to be large, polarizable ones; Cl^-, P and S.

1.2.3. Solution Speciation of Copper and Cadmium.

Ions do not exist as discrete point charges in solution. A simple salt solution of, say, NaCl contains solvated Na^+ and Cl^- ions and by the very fact that they are bearing opposite electrical charges, it can be assumed that they will interact electrostatically.

For Cu(II) in the presence of NH_3, it might be suggested that a $[Cu(NH_3)_6]^{2+}$ complex is formed, considering the Lewis base nature of NH_3. Adding EDTA (Ethylenediaminetetracetic acid), or a similar multi-dentate ligand, to such a system will result in the formation of the [Cu Ligand]$^{X\ (+\ or\ -)}$ rather than the NH_3 complex: such a reaction is entropically

favourable.

A further case could be Cd(II) added to a protein or multi-dentate ligand bearing thiol groups. Cd(II) has a high affinity for electrons, and 'S' (Sulphur atom) is highly polarizable, hence a bond formation between the two will be slightly covalent in form.

From the above examples it can be seen that there are forces acting to push some ions and molecules together, but not necessarily forming a precipitate or a solid phase: to consider solid-solution-solute interactions in terms of total copper, cadmium, or any other solution component, may give a misleading impression of what is occurring.

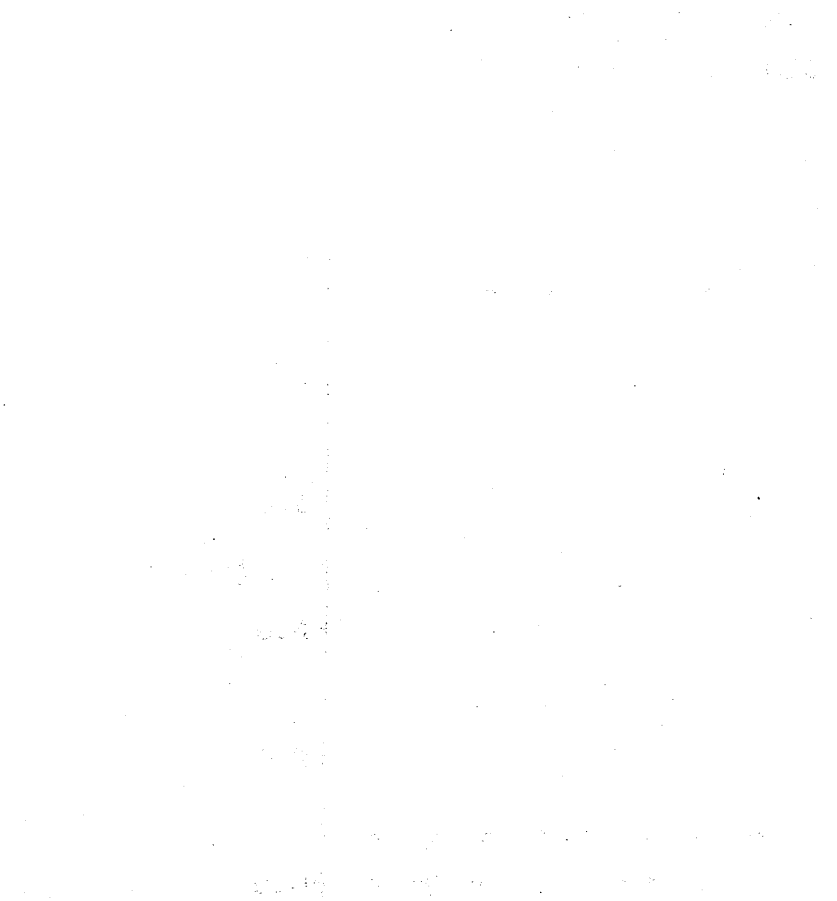
This leads quite naturally into the concept of the chemical species ie. total copper in solution, as measured by, say, AAS (Atomic Absorption Spectrophotometry), comprises hydroxy, carbonate, inorganic and organic ligand species as well as a fraction of uncomplexed Cu(II) - the "free" copper.

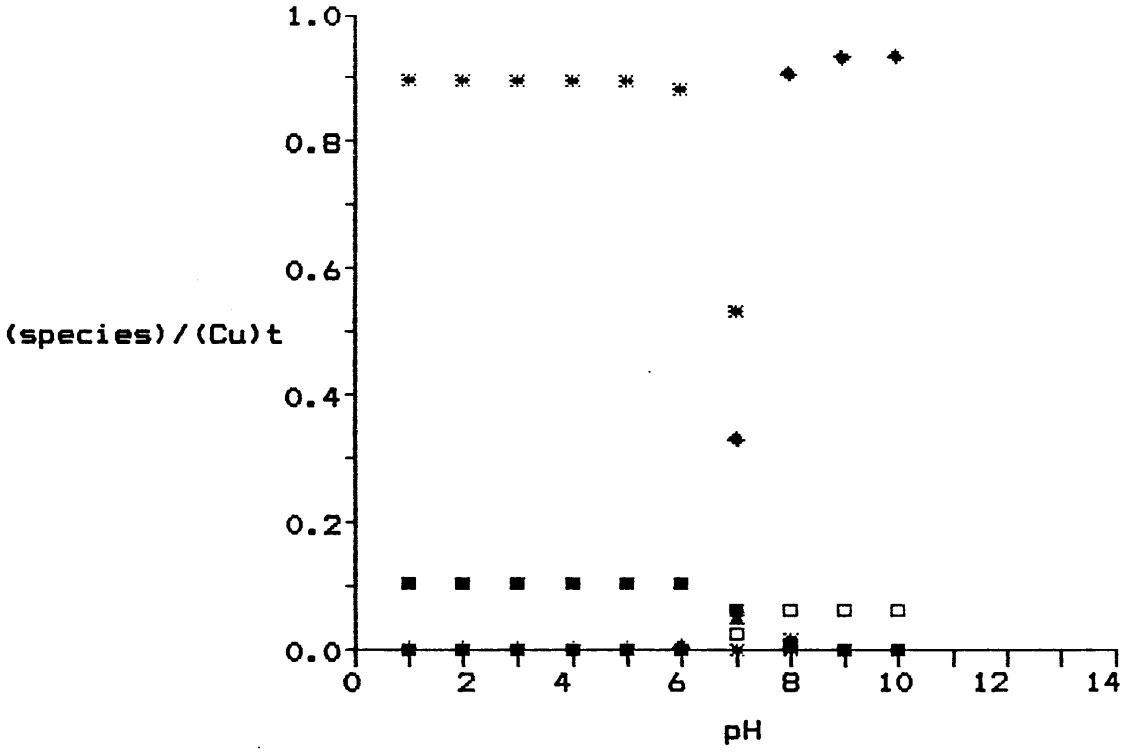
Again, considering a simple salt system, this time $NaNO_3$, at equilibrium with atmospheric CO_2 and containing Cu or Cd, the following distribution diagrams demonstrate changes in solution speciation as a function of pH - figures 1.1. and 1.2..(the equations and computer programmes used to solve this and other speciation systems can be found in appendix 1).

Figures 1.1 and 1.2.

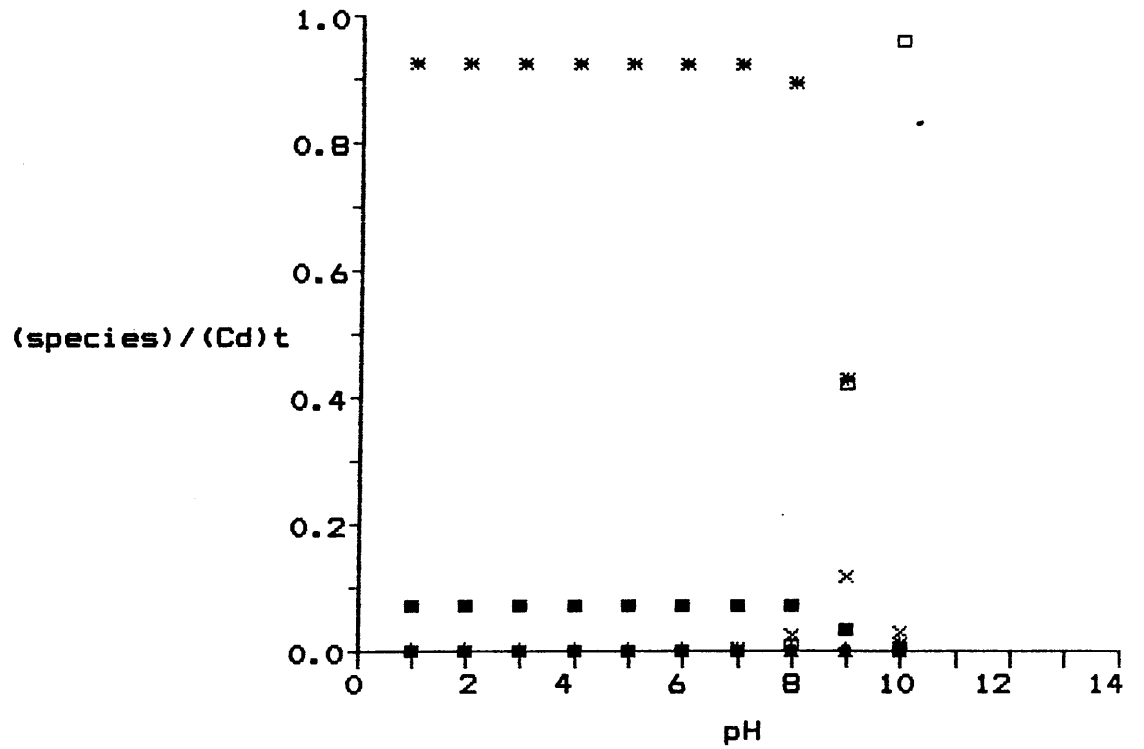
Figure 1.1.; Speciation of Cu in 0.1M $NaNO_3$, $pCO_2 \approx 10^{-3.52}$ atm.

Figure 1.2.; Speciation of Cd in 0.1M $NaNO_3$, $pCO_2 \approx 10^{-3.52}$ atm.





Cu species distribution in NaNO3 (I=0.1).
Cu - * HO1 - tri. HO2 - dia. (NO3)1 - sq.
(NO3)2 - + HCO3 - x CO3 - open sq.



Cd species distribution in NaNO3 (I=0.1).
Cd - * HO1 - tri. HO2 - dia. (NO3)1 - sq.
(NO3)2 - + HCO3 - x CO3 - open sq.

Clearly, for both metals, the "free" ion dominates, except above pH 6 for Cu(II), although at the concentration of NO_3^- used, the nitrate complexes do show a degree of significance.

With such a diversity of species in solution, and doubtless on surfaces, there should be differing degrees of affinity amongst the species for uptake onto solids, however, the only definitive evidence for sorption of species 'x' as opposed to species 'y' from a solution would be spectroscopic, which, at the moment, is not yet feasible in soil solutions.

The concept of speciation is important (from a toxicity point of view this has been demonstrated for Al, Cu and Hg). Some instances where speciation has been shown to be of importance are;

Al - a need to understand the speciation of aluminium has been demonstrated by Helliwell *et al* (1983) due to the mooted toxicity of the hydroxy species.

Cu - Gupta (1988) correctly states that whilst total metal concentrations are good indices of soil saturation, the chemical form is much more important.

Hg - the Minimata incident in Japan in the 1960`s.

Cd - Christensen (1989) points out the necessity of speciation, as complexed Cd has a higher mobility than the free forms.

Whilst the spectroscopic means to study the phenomenon are not yet fully developed and available, calculative and physio-chemical methods can allow us some insight into this branch of chemistry.

Approaches to speciaton are many and various;

(a). Calculative methods;

GEOCHEM (Sposito and Mattigod 1977).

Carbonate species (Tarazona 1988).

(b). Physico-chemical methods;

1. Dialysis (Minnich & M^{C}Bride 1987; Minnich *et al* 1987).

2. Chromatography;

Ion exchange (Camerlynck and Kiekens 1982).

Size exclusion (Gardener *et al* 1982).

3. Electrophoretic mobility (Puella *et al* 1987; Van Dorst and Peterson, 1984).

4. Electrochemical;

ISE`s (Minnich and M^{C}Bride 1987; Minnich *et al* 1987).

ASV (Florence 1977).

5. Chemical extraction (Florence 1977; Sposito *et al* 1982).

1.3. The Sorption Reactions of Copper and Cadmium.

1.3.1. The Sorption Process.

The chemical basis of the reactions of Cu and Cd in soils can be approached in two ways;

(a). Measurements made on individual soil components.

(b). Measurements made on whole soils.

Both approaches work towards the same end, but the former does so by trying to build up to a description of the soil reaction, whilst the latter attempts to describe the scenario by breaking it down into its constituent parts.

Before discussion of the soil reactions of Cu and Cd, we

can obtain some idea of what can and cannot occur chemically in soil via the HSAB (Hard-Soft-Acid-Base) principle of Pearson (Douglas *et al* 1983). This largely qualitative approach to molecular and ionic association can be likened to the rigorously quantitative method outlined in the section of this thesis on speciation (section 1.2.3.). This theory considers ions and molecules in terms of their size and resistance to polarization ie. an ion which is small (or, has a high charge density) and is thus not easily polarized is regarded as 'Hard', the corollary of this is that low charge density species are 'Soft'. The categorization is further qualified in terms of the Lewis acidity/basicity of the ion or molecule in question: negatively charged or lone pair bearing species are Lewis bases, whilst positively charged, or molecules having unfilled bonding orbital(s) are Lewis acids. According to the theory, strong relationships will exist between soft acids and bases or hard acids and bases. On this classification, Cu(II) is a borderline acid, whilst Cd(II) is a soft acid. The following table (1.7.) is taken from Douglas *et al* (1983) and includes many of the ligands which will be present either in soil solutions or on soil surfaces.

Table 1.7. Some Examples of Lewis Bases.

Hard;	NH_3	H_20	HO^-	CO_3^{2-}	PO_4^{3-}	F^-
	RNH_2	ROH	RO^-	SO_4^{2-}		Cl^-
	N_2H_4	R_2O	CH_3C00^-			
			ClO_4^-			
			NO_3^-			

Borderline (table 1.7. continued);

C_6H_5N NO_2^- SO_3^{2-} Br^-

$C_6H_5NH_2$.

(where R is any organic molecule).

A further consideration, in terms of direct ion replacement within a crystalline matrix, will be the ionic radius of the incoming species: table 1.8. provides a list of some major soil cations.

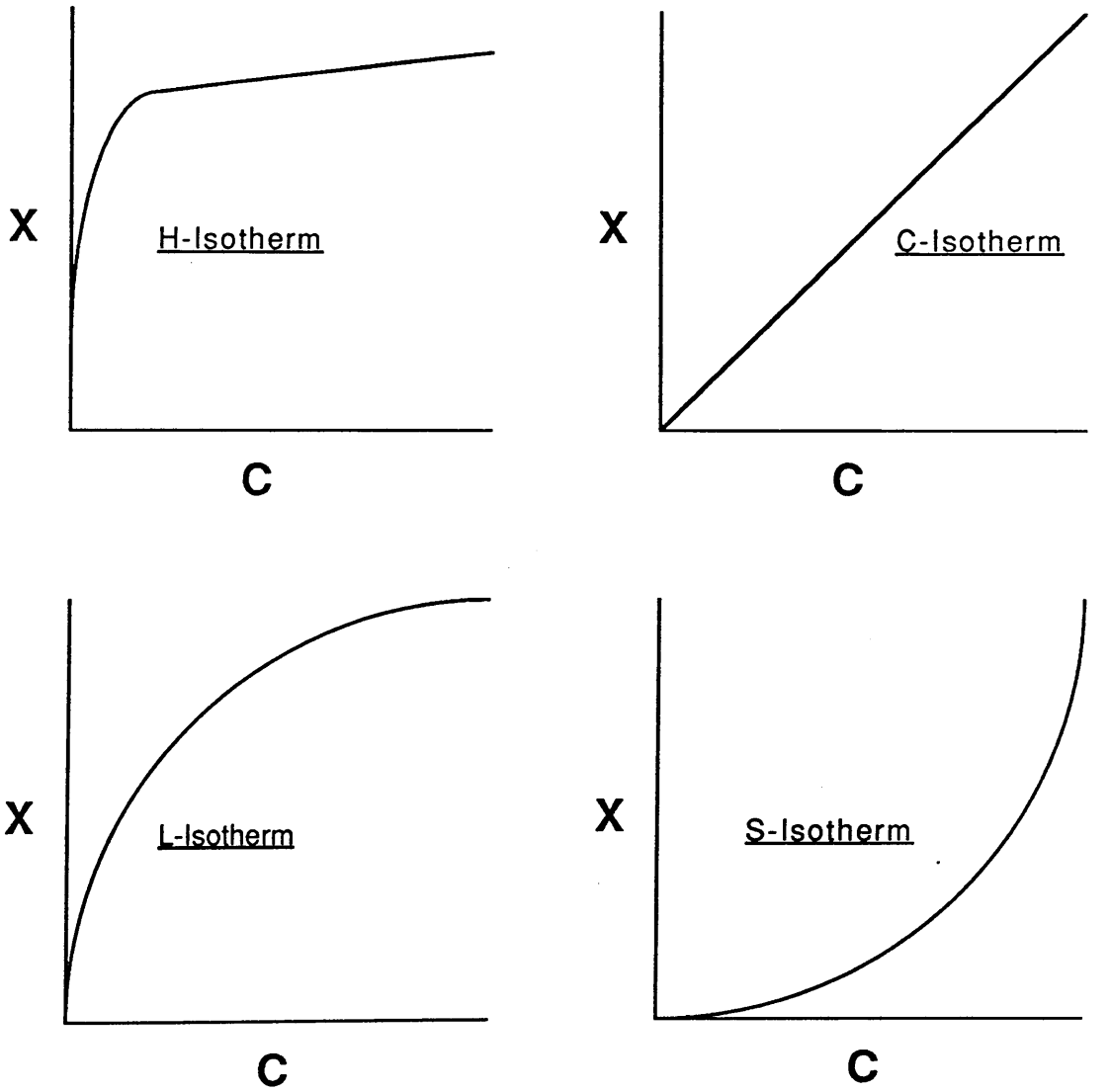
Table 1.8. Ionic Crystalline Radii (in pm) of some soil ions.(Emsley 1989)

Cu^{2+}	72	Mn^{2+}	91	Mn^{4+}	52	Fe^{3+}	67
Cd^{2+}	103	Ca^{2+}	106	Zn^{2+}	83	Al^{3+}	57

1.3.1.1. Qualitative Description of Sorption.

Sposito (1984) suggested the use of the term "sorption" to eliminate any prejudgement of a mechanism from an isotherm. A graph of "amount sorbed" versus "equilibrium solution concentration" may have many forms, which Giles *et al* (1974 a and b). managed to distill down to four main types:

Diagram 1.3. The 4 Fundamental Sorption Isotherms



X = Adsorption density or amount sorbed.

C = Equilibrium concentration.

The H-type demonstrates a surface which has a very high affinity for the sorbate, which falls off sharply at higher concentrations.

The C-type is known as the constant partition isotherm and shows a continual but constant degree of sorption per unit change in the equilibrium concentration. Such an isotherm may be due to the rapid diffusion of molecules of sorbate within the sorbing matrix, or due to the opening out of the matrix, increasing the surface area for sorption: it may also be possible that precipitation is occurring, but the solid phase is heterogeneous and has a continuously variable K_{sp} (Solubility Product).

The L-isotherm is one which is commonly encountered in soil studies, showing a gradual decrease in the avidity of uptake of a surface. Such graphs can sometimes be linearly described by the Langmuir equation:

$$X = \frac{K.X_m.C}{1 + KC}$$

X = amount on surface

C = equilibrium concentration and

K and X_m are (except in the original derivation and definition) curve fitting parameters (for further information, see section 1.3.1.2.).

The S-isotherm shows a surface which has a low affinity for the solute at low concentrations. This may be more easily comprehended if the opposite proposal is considered, that the solution (and its components ie. ligands) have a greater tendency to interact with the sorbate than the surface. An isotherm such as this may be found if there is some soluble organic material which complexes much of the initial M^{n+} and holds it in solution, whilst at higher metal concentrations;

(a). The organic material is flocculated onto the surfaces of particles.

(b). The organic material is saturated, and further additions of M^{n+} go onto surfaces.

1.3.1.2. Quantitative Description of Sorption.

Adsorption isotherms are constructed with the object of data summarization; if a given set of data can be described by a mathematical relationship then we can make predictions of the behaviour of the system under a certain degree of loading. This is one of the most fundamental reasons behind the desire to construct an adsorption isotherm.

Particularly with isotherms of the H and L type, depending upon the time for the experiment, changes can be observed in the slope of the isotherm as C and X increase; it is clear that the conditions under which the material is being removed from solution are changing, and perhaps the isotherm may give some clues as to what is responsible for such variations.

Langmuir (1918) observed that under a given set of conditions, the retention of gases in a single layer on the surface of a solid could be described by the following equation;

$$\Omega = \frac{N_o/N.\ \partial.\ \mu}{1 + \partial.\mu}$$

N = Avogadro's number.

N_0 = the no. of elementary spaces per sq. cm of surface.

∂ = a/v

μ = the no. of gram molecules striking each cm^2/s.

Ω = the no. of gram molecules of gas sorbed per unit of area.

a = proportion of atoms striking surface which condense.

v = rate of evaporation.

As mentioned earlier, this is normally shown as

$$X = \frac{KX_m.C}{1+KC}$$

where X = amount sorbed (correctly, adsorbed).

C = equilibrium concentration.

Xm has been used as an index of the maximum amount which could be sorbed, whilst K has been viewed as being related to the free energy of adsorption.

This equation is essentially derived from first order rate considerations (Mortvedt *et al* 1972).

Some further conditions were that

(a). Monolayer coverage only occurred.

(b). The sorbed species did not interact with one another.

(c). There was no decrease in the free energy of adsorption with increasing coverage.

(d). The sites were homogeneous.

This equation has been widely applied to the soil reactions of cations and anions, but the criteria suggested by the original definition of the equation will probably not be met in the soil, even if we eliminate condition (d) in the form of a multi-site isotherm.

ie. $$X = \frac{K_1.X_m1.C_1}{1 + K_1.C_1} + \frac{K_2.X_{2m}.C_2}{1 + K_2.C_2}$$

However, many workers have used this equation to derive "thermodynamic" bonding constants and laid great emphasis on the "Maximum" parameter as a predictive unit (Shuman 1976; Ryden *et al* 1977; Shuman 1988).

The multi-site isotherm has also been widely applied, with concomitant assumptions being made on the underlying mechanics of the reaction (Ryden *et al* 1977; Shuman 1988).

In a critical examination of the work on phosphate retention of Ryden*et al* (1977), Posner and Bowden (1980)

showed that a single site model could be invoked to describe the sorption which Ryden *et al* (1977) ascribed to a minimum of three sites. In their model, Posner and Bowden allowed for the changes in the surface potential and charge which would result from the sorption of P.

Sposito has examined the Langmuir equation very thoroughly from theoretical and chemical points of view (Sposito 1981, 1982 & 1984; Veith & Sposito 1977), and from this body of work the following statement regarding the Langmuir equation can be made: Under no circumstances can a mechanism of retention be implied from data conformity to the Langmuir equation. This is demonstrated by the facts;

(a). Where the Langmuir equation results in a curve, such that K_d decreases as the amount sorbed increases and eventually becomes zero, such a curve can always be resolved and described by the "two-surface" approach.

(b). That precipitation phenomena may be described by this equation.

These facts, allied to the discovery of Posner & Bowden (1980) underline the redundancy of any mechanistic interpretation which is solely based on the applicability of any forms of this equation, but Kinniburgh (1986) and Shuman (1988) still referred to the multi-constant Langmuir as being "multi-site".

The van Bemmelen-Freundlich equation is the main equation applied to soil-sorbate studies. This equation presumes an exponential decrease in the free energy of adsorption as surface coverage increases and has the form:

$$X = aC^{\beta}$$

Where X is the amount adsorbed, C is the solution

concentration at equilibrium and a and ß are curve fitting parameters. This equation occurs in many adapted forms, particularly those of Sibbensen (1981), but these simply introduce more curve fitting parameters into the equation.

Sposito (1980, 1981) has shown that this isotherm may be regarded as an equation which summarizes the presence of several groups of sites, which in isolation could be described by Langmuir equations. The factor, ß, is an index of the heterogeneity of the sites under observation: the values tend to be less than or equal to one. Where ß = 1.0, the sites are homogeneous, and the sorption may be described by the Langmuir equation. The more ß falls below 1.0, the greater the spread of types of sorbing areas.

Two stage van Bemmelen-Freundlich isotherms have commonly been noted in trace-metal-soil studies (Jarvis & Jones 1980; Jarvis 1981; Elrashidi & O'Connor 1982) and, in a manner similar to that used with the Langmuir equation, this has been attributed to a change in the bonding sites involved in uptake.

No theoretical dissection of the "two-surface" Freundlich has been reported, but Ritchie and Jarvis (1986) have attempted to relate the break in the adsorption gradient to changes in the speciation of the soil solution. Since the van Bemmelen-Freundlich relationship is logarithmic, it would be expected that only major changes in the nature of the relationship between the solution equilibrium concentrations and the amounts sorbed would be shown up by this equation, and that the progression from high to low energy binding sites would be relatively subtle and that curves would result. This is indeed what occurs, and the splitting of the graph into two portions and ascribing the change in behaviour to different affinities of binding sites is arbitrary and the only justification for doing so is to

simplify the data summary.

If this equation had any of the assumptions associated with it that the classical Langmuir has, then, as with the Langmuir equation, an absence of a straight line relationship must nullify all of them: for the correct description of sorption by this equation, a straight line relationship is an immediate requirement.

As the van Bemmelen-Freundlich is equivalent to the weighted sum of many Langmuir equations, then the lack of any mechanistic basis for the Langmuir pertains to the van Bemmelen-Freundlich too.

Sposito, in his book "The Surface Chemistry of Soils" (1984) made the statement which should be heeded by anyone attempting to describe sorption data by these isotherms; that, without *a priori* reasons for believing so "the adherence of experimental sorption data to an adsorption isotherm equation provides no evidence as to the actual mechanism of the sorption process in a soil".

1.3.2. Measurements Made on Soil Components.

These studies involve the use of discrete portions of soil materials (clays, oxides, organic matter) and describing the reaction of Cu and Cd with these components. From such an approach, it may be possible to suggest which fractions of the soil matrix contribute most to the removal of Cu and Cd from solution.

McLaren and Crawford (1973b) performed such a study with copper and Mn-oxide, organic matter, Fe-oxide and Montmorillonite, finding that for pH`s less than 5, the order of affinity for the Cu was;

MnO_2>organic>Fe-oxide>>>Montmorillonite.

Above pH 5 the first three showed an almost identical

affinity.

Eriksson (1988) looked at the influence of clay, organic matter and time on Cd removal from solution and found that this was enhanced by increasing the level of organic materials, and that most of the extra Cd removed by this additional organic matter was sequestrated in a form non-exchangeable to 1M CH_3COONH_4,pH 7. Clay had a minimal influence on Cd uptake.

In an effort to quantify the individual reactions, some authors quote conditional stability constants for the system which they studied eg.

for Cu on Birnessite (∂-MnO_2);

$$Cu^{2+}_{(aq)} + MnO_{2(s)} \rightleftharpoons [Cu\text{-}MnO_2]^{2+}_{(s)}$$

$$K = \frac{[Cu\text{-}MnO2]^{2+}_{(s)}}{[Cu^{2+}]_{(aq)} \cdot [MnO_2]_{(s)}}$$

where the equilibrium constant, K, is the Conditional stability constant, given that its value will be dependant upon the pH, ionic strength, and concentrations of the solute and sorbent used. Some of those determined are listed below (table 1.9.).

Other workers have, rather than determining stability constants, suggested selectivity sequences to demonstrate relative affinities. Examples of these are shown in table 1.10.

Table 1.9. Some Soil Component Stability Constants.

Element	Sorbent material	pH	I	logK	Reference
Pb	∂MnO_2	6.0	0.1	6.25-6.40	Balikungeri and Haerdi (1988).
Cu	∂MnO_2	6.0	0.1	5.55	*ibid.*
Cd	∂MnO_2	6.0	0.1	5.00	*ibid.*
Zn	∂MnO_2	6.0	0.1	4.50	*ibid.*
Cu	soluble	/	/	K_1 13-14.8	Van den Berg *et al.*(1987).
Cu	organic	/	/	K_2 11.5-12.1	*ibid*
Zn	matter	/	/	8.6-10.6	*ibid*
Cu	fulvic acid	5.0	0.1	8.67-8.76	Schnitzer and Skinner (1966).
Cu	Soil	/	0.1	7.19-7.52	Stevenson (1977).
Cd	humic	/	0.1	5.17-6.06	*ibid.*
Pb	materials	/	0.1	7.00-7.36	*ibid.*
Cu	Root	5.0	0.1	4.1	Mench *et al* (1988)
Pb	exudates	5.0	0.1	3.8	*ibid.*
Zn	m.wt. < 1000	5.0	0.1	3.4	*ibid.*

Table 1.10. Some Selectivity Sequences for Soil Materials in Association with Heavy Metals.

Sorbent	I	Selectivity Sequence	Notes	Reference.
Aluminium oxide plus Tannic acid.	0.1	Cu > Zn		Goh *et al* (1986)
Hydrous Aluminium oxide.	1.0	Cu > Pb > Zn > Ni > Co > Cd > Mg > Sr		Kinniburgh *et al* (1976)
Hydrous Iron oxide.	1.0	Pb > Cu > Zn > Ni > Cd > Co > Sr > Mg		*ibid.*
Hydrous Iron oxide.	0.1	Zn > Cd > Ca	in presence of PO_4^{3-}	Kuo (1986).
Goethite	0.075	Cu > Pb > Zn > Co > Cd		Forbes *et al* (1976)
Montmorillonite	0.01	Cu > Cd	constant partition model gradients ∞ pH.	Inskeep, Baham (1983).
Calcite	/	Cd > Mn > Zn > Co	same order as ionic radii.	Comans, Middleburg (1987).

1.3.2.1. Copper and Cadmium uptake on to Calcite.

Principally because of the similarity of their ionic radii (Cd - 103 pm, Ca - 106 pm) it might be expected that fairly specific reactions occur between Cd and $CaCO_3$, and, indeed, this is what has been found. Papadopolous and Rowell (1988) observed that at low concentrations of Cd^{2+}, ($<10^{-6.5}$M), adsorption appeared to be the principal mechanism of uptake The adsorption was classed as a 'C' type, (Giles *et al*,1974 a and b).-there was no pH change, no change in $[Ca^{2+}]$ and the isotherm was almost linear. At higher concentrations, the affinity of the Calcite for Cd was still very high, however the process appeared to change, the pH fell and $[Ca^{2+}]$ rose indicating an exchange

$$CaCO_{3(s)} + Cd^{2+}_{(aq)} \rightleftharpoons CdCO_{3(s)} + Ca^{2+}_{(aq)}$$

or a coprecipitation

$$CaCO_{3(s)} + HCO^{3-}_{(aq)} + Cd^{2+}_{(aq)} \rightleftharpoons CdCO_{3(s)} + CaCO_{3(s)} + H^{+}_{(aq)}$$

Given the changes in pH and $[Ca^{2+}]$, the latter process would appear to be the more likely to occur. The distribution coefficients would tend to suggest the formation of a solid solution at low concentrations. According to Stumm and Morgan (1981), such a situation leads to increased activity of the co-precipitant, and, hence, reduced solubility leading to the formation of a new solid phase.

Farley *et al* (1985) proposed a model which should describe the situation described above; the Surface Precipitation Model. This is a solid-solute version of the BET (Branauer, Emmet and Teller) equation, which describes the adsorption and condensation of gases on to solid phases. The condensation stage is replaced by the concept of a newly forming solid phase of continuously varying

composition, until it reaches that of the sorbing species precipitate, at which point, the level of the sorbing species in solution becomes a function of the solubility product of the newly formed phase. Farley *et al* (1985) applied this model to iron oxide and found that it could describe the sorption of Cu, Cd, and Zn. Comans and Middleburg (1987) have applied this model to calcite and demonstrated its applicability for Cd, Zn, Mn and Co uptake. The same principles have been utilized by Davis *et al*(1987) for Cd uptake on to calcite.

In the latter reference and in a paper by McBride (1980a), a two-stage reaction was noted, and presented as further evidence for solid solution formation. Papadopolous and Rowell (1989), this time examining the chemistry of the reactions of Cu and Zn with synthetic and 'natural' Calcite, proposed that the surface coverage of Cu is incomplete at the point at which precipitation begins, and that the precipitate is not a uniform $CuCO_3$ matrix. It may be a hydroxide or oxide layer, both of which have lower solubilities than $CuCO_3$. The observed heterogeneous precipitation distribution coefficient was very different from the theoretical, which suggested that there was no smooth progression from adsorption to precipitation (via solid solution formation) of the carbonate.

As Sposito (1984) has pointed out, the only direct way of knowing whether electrostatic or covalent bonding has occurred at a surface is by spectroscopic methods: Davis *et al* (1987) attempted this, but found that the Cd levels were below the detection limits of the methods employed (XPS - X-Ray Photoelectron Spectroscopy and AES - Auger Electron Spectroscopy).

For Mn uptake on to Calcite, McBride (1979) has used ESR

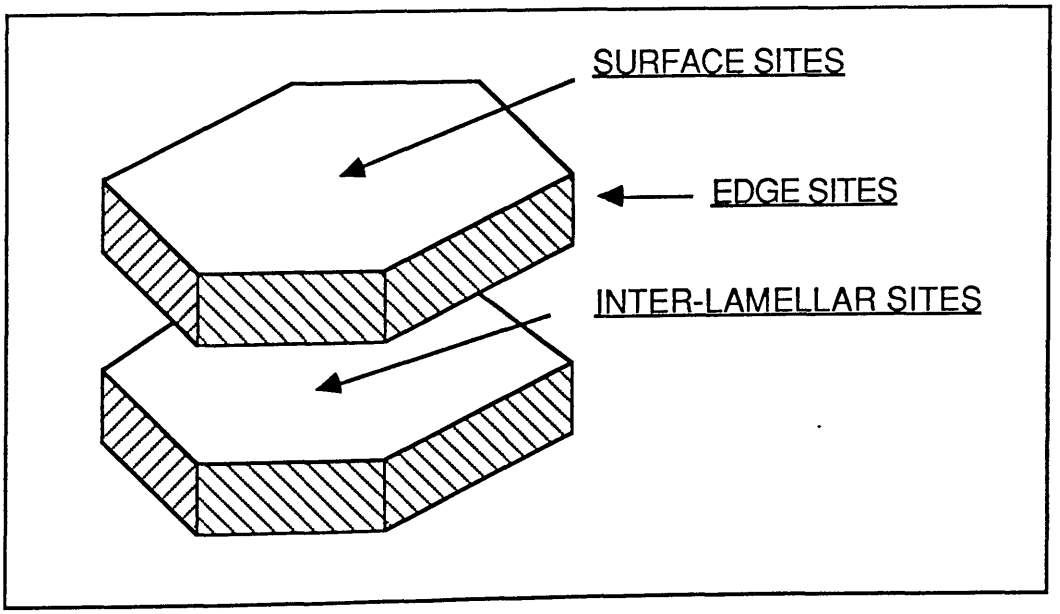
(Electron Spin Resonance Spectroscopy) to definitively show the presence of $MnCO_3$ on a $CaCO_3$ surface.

1.3.2.2. Copper and Cadmium Uptake on to Clay Surfaces.

As mentioned earlier, McLaren and Crawford (1973b) found that the clay component of soil (Montmorillonite in this case) made very little contribution to the retention of Cu(II), relative to oxides and organic matter, whilst Eriksson (1973) demonstrated that clay additions to soil little influenced its ability to retain Cd (the type of clay used is not specified).

In spite of this, numerous studies have been performed upon various clays to elucidate preferences of clays for metallic ions and the factors influencing their retention.

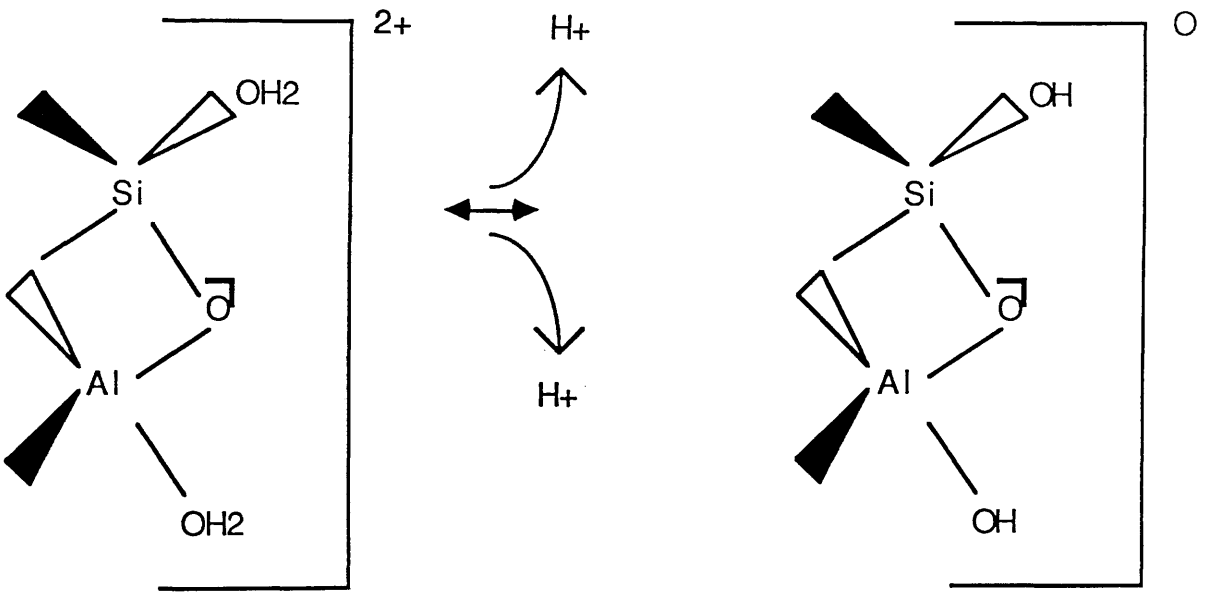
Ziper *et al*(1988) considered Cd sorption on to five clay types. Idealized clay particles give rise to three bonding site types;



The surface change is due to isomorphous substitution of

Al^{III} for Si^{IV} in silica sheets and Mg^{II}/Fe^{II} for Al^{IV} in Alumina sheets: by its very nature, this charge is fixed. The inter-lammellar charge is of the same nature, but by the packing of the units this charge is sheltered from the solution around it.

The clay edges are more heterogeneous in their nature and are liable to protonation/deprotonation effects.



Hence, the influence which these sites have upon the sequestration of ions from solution will be linked to the pH of the solution.

Ziper *et al* (1988) found that edge and plane charge density predominates in Cd sorption and that the avidity with which Cd was removed from solution was chiefly a function of the CEC (Cation Exchange Capacity). In terms of the selection of Cd by the clays, the order was;

Vermiculite > Montmorillonite > K-Vermiculite > Biotite > Kaolinite.

Puls and Bohn (1988) found that the hydroxy edge sites of

Kaolinite were important in the Cd sorption process, and that this could be explained in terms of the HSAB principle of Pearson; if edge sites are considered to be soft bases, the following selectivity sequence applies to Kaolinite

$$Cd > Zn > Ni$$

$$\longrightarrow$$

Increasing hardness

Garcia-Miragaya and Page (1977) looked at the influence of the competing cation and Cd uptake from solution, and showed that this was related to;

(a). the valency of the competing ion

(b). the pH of the suspension.

The order of decreasing Cd removal from solution was;

Na-Mont. > K-Mont. > Ca-Mont. >Al-Mont.

pH 7.3 pH 7.2 pH 6.7 pH 4.6

The Al-Montmorillonite Cd isotherm was the only one which exhibited a negative $[Cd]_{ads}$ intercept indicating that in acidic conditions (H^+ and Al^{3+} in solution) there was a marked reduction in the affinity at the surface for Cd, possibly by Al^{3+} or H^+ competition. Garcia-Miragaya and Page (1977) considered the influence of the ionic strength and inorganic ligands on Cd-sorption by Montmorillonite and found that even "non-complexing" ligands like ClO_4^- could decrease Cd (II) in solution, whilst Cl^- systems showed a very great decrease. Despite a relatively high K_{ass}(Association Constant), CO_3^{2-}-Cd^{2+} complexes did not have a great influence on the total level of Cd in solution; slightly less was taken up from SO_4^{2-} than ClO_4^- at similar ionic strengths, but it must be borne in mind that there would be a lower concentration of SO_4^{2-} compared to ClO_4^- at equivalent ionic strength.

Farrah and Pickering (1976 a and b) looked at the interaction of three clay types with Cu as influenced by

solution ligands: En (Ethylene Diamine), EDTA (Ethylenediaminetetracetic Acid), Mg^{2+}, Ca^{2+}, Cyanide and NH_4^+ in solution all diminished the extent of removal of Cu from solution. They observed Cu precipitation on Montmorillonite, at a much lower pH than that expected for CuO and reasoned that it was more likely to be $Cu(HO)_2$, due to a relative excess of 'HO' (in the form of surface hydroxyls) on the edges and faces of the clay material.

Inskeep and Baham (1983) examined the adsorption of Cd and Cu on to Montmorillonite. Over the range of 0.1 - 50 μM Cu and Cd they found that uptake was largely independent of pH, over the range 4 - 8.5, with Cu showing slight sensitivity to changes in pH. Uptake was, however, pH reversible, indicating a degree of competitiveness, but as this followed the same isotherm regardless of the direction of approach (from acidic or alkaline conditions), it could be inferred that the Cu and Cd ions are held on easily accessible surface sites, ie. that they had been adsorbed.

Conclusions which may be drawn from this body of work are:

(a). Oxide and organic matter are the main sites for Cu and Cd.

(b). Calcite has a particular affinity for Cd which may be considered in terms of solid-solution formation and co-precipitation.

(c). The solution composition; pH, I and presence of organic and inorganic ligands, will exert an influence over the amount of Cu and Cd removed from solution.

(d). Overall, Cu retention is greater than Cd.

1.3.3. Soil Based Studies on Copper and Cadmium.

Whilst model oxides, carbonates and clay particles are relatively well-characterized solid phases, in soil there is an uncertain mixture of all of these, with organic matter added in to further complicate matters.

There are two main approaches to the study of soil-metal ion interactions;

(a). The adsorption isotherm

(b). The fractionation scheme.

The adsorption isotherm is universally applied to cations, anions and organic materials, nominally charged or otherwise. In its simplest form it attempts to describe a relationship between the amount of material in the equilibrium solution and the amount of material adsorbed on to a solid phase. This is one of the most basic statements and measurements which can be made about a soil-solution system, but even this is flawed.

Adsorption is strictly a surface two-dimensional phenomenon. "Adsorption" is usually measured as the decrease in concentration, over time, of a given substance in equilibrium with a given solid phase

ie. for Cu; $[Cu^{2+}]_{Adsorbed} = [Cu^{2+}]_{Initial} - [Cu^{2+}]_{Equilibrium}$

Disappearance from solution is no criterion on which to base the assumption that the mechanism responsible for sequestering Cu^{2+} (or Cd^{2+}) from solution is adsorption. This removal from solution encompasses adsorption, absorption and precipitation, so, without very strong auxiliary evidence, the ultimate being spectroscopic surface analysis, there is very little *prima-facie* evidence to suggest a given mechanism is responsible for the observed depletion in solution concentration of Cu, Cd or any other solution species.

Having looked at the basic tools of description of the solid-solute interaction, it is aposite to consider what other researchers have found when examining copper and cadmium in this context. These are summarized in tables 1.11. and 1.12.

Table 1.11. Summary of Literature Soil-Cd Interactions.

	Soil : Solution	Background Electrolyte	Concentration* Range	Equation Fitted
Garcia-Miragaya & Page, 1978	1 : 800		4 - 42 µM	Freundlich
Soon , 1981.	1 : 12.5	0.05M $Ca(N0_3)_2$	1.3 - 26.7 µM	Mod. Freundlich
Christensen, 1984	1 : 50	10^{-3}M $CaCl_2$	0.52 µM at eq.	Freundlich
O'Connor *et al*, 1984	1 : 1	0.005M $CaCl_2$ 0.05 M $CaCl_2$ 0.005M $CaSO_4$ 0.005M $Ca(Cl0_4)_2$	0.003 - 356 µM	Freundlich
Jarvis & Jones, 1980	1 : 10	0.002M $CaCl_2$	0 - 40µM	2-Stage Freundlich
Levi-Minzi *et al*, 1976	1 :50		890 - 2670µM	Langmuir
Narvot *et al*, 1978	1 : 25	0.01M NaCl	0 - 4450µM	2-Stage Langmuir
Cavallaro & M^{c}Bride, 1978	3 : 500	H_2O, 0.01M $CaCl_2$	38 - 800µM	Langmuir

*For comparison's sake, all the concentration ranges have been adjusted to the level of 1 : 25, as this is the ratio at which my work was carried out.

Table 1.12. Summary of Literature Soil-Cu Interactions.

	Soil : Solution	Background Electrolyte	Concentration* Range	Equation Fitted
Kurdi & Doner 1983	1 : 20	0.02M $CaCl_2$	63 - 2560 µM	Freundlich
Jarvis, 1981	1 :10	0.01M $CaCl_2$	0.2 - 400 µM	2-Stage Freundlich
Cavallaro & M^{c}Bride 1978	1 : 250 1 :125	H_2O, 0.01M $CaCl_2$	38 - 1250 µM	Langmuir
Petruzzelli *et al*, 1985	1 : 4	0.005 -0.05M $CaCl_2$	1.3 - 1890 µM	Langmuir
Gambus, 1987	1 : 10	0.015M $CaCl_2$	1.3 - 1890 µM	2-Stage Langmuir
M^{c}Laren *et al*, 1983	1 :10	0.05M $CaCl_2$	0 -12.6 µM	CvX is Linear
Van Bladel *et al*, 1988	1 :125	H_2O, 10^{-2} $NaClO_4$, 3.3 and 20mM $CaCl_2$	40 - 1260 µM	Langmuir

*For comparison's sake, all the concentration ranges have been adjusted to the level of 1 : 25, as this is the ratio at which my work was carried out.

Such is the disparate nature of these studies, that any comparison is difficult. The only patterns which can be discerned are that, for cadmium, as the concentration range of the study increases, there is a shift of data description from the Freundlich to the Langmuir. If we consider the restriction on the applicability of the van Bemmelen-Freundlich (Sposito 1984), that the gradient term is an indication of the site heterogeneity, and that its approach to unity implies homogeneity and hence applicability of the Langmuir isotherm, then it can be said that the trend displayed by the cadmium studies is indicative of increasing regularity of the surface sites, possibly because the specific sites are all occupied, and, as the K_d (Distribution Coefficient) value for specific sites may be many orders of magnitude greater than those for the more prolific exchange sites, there may be a change to mass action displacement of the major soil cations from ion-exchange sites.

The copper studies show what may be a progression in the dominance of sites removing Cu^{2+} from solution; from a limited group of specific, homogeneous sites, to a broader group and finally to a degree of homogeneity at higher concentrations, the Freundlich isotherm managing to describe the changes in site specificity over wide concentration ranges.

It must be borne in mind that these are only very broad generalizations.

1.3.4. Factors Influencing the Reaction of Copper and Cadmium with Soils.

As mentioned in a previous section (1.2.3.), in the presence of inorganic and organic ligands, there is the possibility of complexation and ion-pairing. Such behaviour, which was graphically shown in that section is also pH dependent, thus, it may be presumed that these parameters will be influential in the retention of Cu and Cd by soil.

Among the other factors which will exert some control over Cu and Cd uptake will be the nature of the soil materials (oxides, clays and organic matter), the presence of other ions in solution (competitive effect, H^+ influence) and the time with which both elements are in contact with the sorbent.

1.3.4.1. Influence of Soil Composition.

As expected from the previous discussion (section 1.3.2.1.), Calcareous soils have been shown to have a very high affinity for Cd (Estan *et al* 1987), possibly leading to the formation of a discrete solid phase (Santillan-Medrano & Jurinak 1975). In non-Calcareous soils, aside from the fairly obvious effect of increasing surface area (Narvot *et al* 1978), the main influence on Cd uptake is the cation exchange capacity (Estan *et al* 1987). Adding organic matter to soils tends to influence the CEC in a positive manner, and hence the retentive capacity for Cd is related to the amount of organic matter and the CEC (Levi-Minzi *et al* 1976; Garcia-Miragaya & Page 1978; Eriksson 1988). Elliott *et al* (1986) noted a reversal in the trend of their uptake series (Pb > Cu > Zn > Cd) on moving to soils with higher organic matter contents: (Pb > Cu > Cd > Zn),

indicating the relative importance of organic matter in the retention of Cd. Soon (1981) has pointed out, though, that although organic matter additions may enhance the CEC, the sorption of such materials on to solid surfaces may alter its exchange sites to such a degree that the expected increase in sorbing capacity brought about by the organic matter is somewhat tempered.

Goethite (Garcia-Miragaya & Page 1978) and "free" Haematite (Jarvis & Jones 1980) have also been suggested as surfaces having a role in Cd adsorption.

M^{c}Laren and Crawford (1973a) suggested the major involvement of manganese oxides and organic matter in determining the nature of soil-Cu reactions, which was supported by subsequent work (M^{c}Laren *et al* 1983). Kurdi and Doner (1983) also found a relationship between Cu and Mn oxides and other protonated sites (including organic and oxide moieties). Shuman (1979), using a sequential extraction procedure, proposed the following order of importance for soil-copper interactions:

Organic matter > Clay > Silt > Sand > Oxides > CEC.

Whilst M^{c}Laren and Crawford (1973a) deduced the following order:

Clay > Organic matter > Oxides > CEC

but managed to find a significant relationship between "free" manganese oxides and copper.

In a study examining both Cu and Cd, Abd-Elfattah and Wada (1981) suggested that the order of affinity should be:

Iron oxides, > Allophane, > Humus, > Montmorillonite
Halloysite Imogolite Kaolinite

However, the conclusion reached by Brown *et al* (1983) for Cd, Zn, Ni, Pb and Cu was that the mobility of heavy metals in soils was independent of any of the measured soil characteristics (organic matter, CEC etc.). This view, at

low level concentrations of Cu has found some support from Jarvis (1981) and M^{c}Laren *et al* (1981).

1.3.4.2. Influence of Competing Ions and Solution Composition.

Christensen (1987a & b) has extensively studied the influence of other heavy metals upon Cd uptake by soils, and concluded that Zn demonstrated the greatest depressing influence. Cobalt and nickel also showed an effect. A mixture of chromium, copper and lead additionally diminished the retention of cadmium, although no attempt was made to specify any individual elements' responsibility.

The only other major cation effect on Cd relations with soil has been shown by high levels of Ca, and this has usually been interpreted as evidence for the presence of Cd on CEC sites (Christensen, 1984; Jarvis & Jones, 1980; Narvot *et al*, 1978; Petruzzelli *et al*, 1985).

Lodenius and Autio (1989) observed that a salt mixture of Ca^{2+}, Na^{+}, SO_4^{2-} and NO_3^{-} enhanced the mobility of Cd in soils in loading experiments, more so than changing the pH to a more favourable one.

The affinity of Cl^{-} as a ligand for Cd has been stated earlier and its influence has been studied in mobility and uptake experiments. O'Connor *et al* (1984) compared Cd sorption in similar concentrations of ClO_4^{-}, Cl^{-} and SO_4^{2-} and found only slight differences in uptake ($SO_4^{2-} > ClO_4^{-} > Cl^{-}$). Using a (10 fold increase of Cl^{-} concentration reduced uptake significantly .When considering the uptake in terms of Cd activity (ie. eliminating ionic strength and pH differences) the high Cl^{-} line could not be made to coincide with the lower concentration Cl^{-}, ClO_4^{-} or SO_4^{2-} lines. This could be demonstrating an additional factor in the reduction

of Cd^{2+} uptake (Ca^{2+} competition) or may simply be showing the limitations of the GEOCHEM (Sposito and Mattigod 1977) program used to calculate (Cd^{2+}) free. Herms and Brümmer (1984) showed that Cd uptake onto soil decreased in the following order of solutions:

$$H_2O >> NaNO_3 >> NaCl \geq Ca(NO_3)_2$$

Which implies an equal effect of Ca competition and Cl^- complexation in the reduction Cd sorption.

Doner (1978) looked at the influence of Cl^- from a leaching point of view, and found that the movement of Cd in soil columns was greatly enhanced by the presence of chloride ions.

The importance of organic matter in the solid phase has been mentioned, with respect to Cd retention. The solution phase forms may also be implicated as being factors in enhancing solution levels of Cd. Neal and Sposito (1986) ably demonstrated this feature by showing that Cd uptake followed an S-shape isotherm in sludge-amended soil, but on removal of organic matter the uptake pattern followed an L-shaped isotherm.

Little Cu is found in the "exchangeable" fraction of soils (M^{c}Laren & Crawford 1973a) and thus we would expect that only those cations which have an affinity for the more specific sites in the soil can compete/displace Cu to any degree. Petruzzelli *et al* (1985) demonstrated that Ca at high concentrations could reduce Cu uptake. This could be either from a mass action, competitive point of view, or from a flocculating effect of Ca, reducing the effective surface area of the soil.

Kurdi and Doner (1983) have shown a lack of ability of Zn to compete with Cu, even when the initial Zn concentration was ten fold that of the copper.

van Bladel *et al* (1988) looked at the anion effect on Cu uptake and found that, much as expected from the available data on stability constants, chloride was most effective with ClO_4^- and H_2O respectively poorer (this study though compared $NaClO_4$ with $CaCl_2$, so part of the effect may be Ca competition).

Doner (1978) also found an enhancing effect on mobility of Cu due to Cl^-, but not a very great one.

1.3.4.3. Influence of pH.

Clay edges, oxides and organic matter all bear functional groups which respond to pH in a way which may be represented by an acid dissociation constant;

$$R\text{-}OH \rightleftharpoons R\text{-}O^- + H^+ \quad \text{where } K = \frac{[RO^-].[H^+]}{[ROH]}$$

where R is a surface atom.

In an analogous fashion to the principle of le Chatelier, an increase in the pH of such a system will tend to "drive" the equilibrium to the right hand side of the equation, and vice versa for a drop in pH.

Thus, the pH of the equilibrium system will influence the proportions of positive and negative sorption sites within the soil material.

At one particular pH, there will be equal amounts of positive and negative charges on the soil, and this is defined as the Point of Zero Charge (P.Z.C.). In very general terms, the surface is positively charged at pH < P.Z.C and negatively charged at pH > P.Z.C., cation retention being diminished by the former situation and enhanced by the latter.

P.Z.C. for as heterogeneous a material as soil is a macroscopic concept, and so, at pH < P.Z.C., negative sites will still be present, thus the sorption of metal ions at pH's

below P.Z.C. should not be unexpected.

The trend of diminishing avidity of uptake with decreasing pH is demonstrated for Cd by Lodenius and Autio (1989) in both a peat soil and a sandy soil (curiously, this is reversed in the sandy soil by reducing the temperature of the equilibration to 5°C).

The discussion of P.Z.C. covers changes in surface speciation, the variation of pH will also produce changes in the solution speciation, and it is possible that the sorption of some of these hydrolysis products may be more favourable than their simple aquo forms. The work of Cavallaro and M^{c}Bride (1980a) has shown that Cd uptake is far less pH dependent than Cu uptake, which reflects their hydrolysis constants (Cu pK_1=7.70, Cd pK_1=10.10 (Lindsay, 1979))

Herms and Brümmer (1984), though, showed that the relationship between $[M^{2+}]_{solution}$ / $[M^{2+}]_{sorbed}$ drops sharply with pH for Cd, but not so for Cu.

So, despite the relative pH insensitivity of Cd in solution, it seems to respond to changes in surface speciation, sorption becoming more favourable with increasing pH. With Cu, the relatively pH labile solution speciation in association with the changes in surface speciation do not result in such a sharp decline in solution Cu levels as might be expected. Several authors have demonstrated that increased pH does enhance the uptake of Cu and Cd from solution, but that it does not necessarily proceed to precipitation of an oxide or hydrous oxide. Kuo and Baker (1980), M^{c}Laren *et al* (1983) and McBride and Blasiak (1979) have shown that for Cu, Zn and Cd, the relationship of equilibrium pH to the metal concentration is more complex. As the pH of soil is increased, organic

matter becomes increasingly soluble (probably due to electrostatic repulsion and diminution of Hydrogen bonding between the organic and inorganic components of the soil). What the above authors demonstrate is that when this enrichment of the soluble organic component occurs, organo-metallic complexes form in solution, and depending upon the strength of this sequestration, precipitation is delayed until much higher pH values than expected. The behaviour observed is typified in figure 1.4.

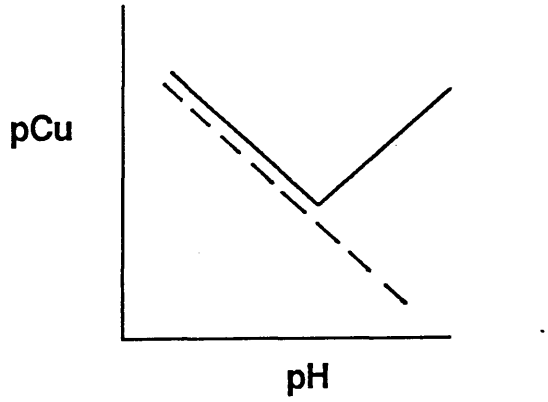


Figure 1.4. Change in Cu Activity with pH.(after McBride and Blasiak 1979).

M^{c}Bride and Blasiak (1979) showed that the plotting of total [Cu^{2+}], on the y-axis of the above graph, produced the `V` shape as expected, but when (Cu^{2+}) (copper activity) was substituted, it declined in a straight line (--- above), direct proof of the role of changing speciation in relation to metal uptake.

Cavallaro and M^{c}Bride (1978) showed that sorption of Cu and Cd resulted in a drop in the suspension pH, but when this experiment was repeated in the presence of 10^{-2}M $CaCl_2$, the pH change was removed and sorption became almost pH independent: this demonstrates that the highly specific

uptake of Cu and Cd, against the blocking of non-specific sites by Ca, need not result in the displacement of protons.

1.3.4.4. Influence of Time.

Depending upon the rate at which sorption (or precipitation) occurs, the time with which a solution is in contact with a solid phase will greatly influence the extent to which a reaction is observed to occur. A list of the various times used by a selection of authors is shown in table 1.13.

Table 1.13. Some Literature Equilibration Times.

	Equilibrating time (hours).			
	0-12	13-24	25-48	49+
Cd no.of studies found	2	7	4	2
Cu	2	6	1	3

No. of studies consulted = 27.

From the studies covered in this table it can be seen that the influence of time is not very consistent, and probably reflects the conditions under which the study was conducted and the soil type used. If the very long equilibration times are excluded, an average figure for short term equilibration studies can be determined:

Cu - 20 h (S=70%)

Cd - 27 h (S=63%).

Certainly, most uptake occurs within minutes of the establishment of contact between the solution and the solid

phases, the majority being sorbed within 24 hours.

1.4. Overview of Chapter 1 and Thesis Aims.

Summarizing the previous sections, the following generalizations can be made;

(a). In agreement with Papadopoulos and Rowell (1988) and McBride (1980), soils with high Calcite contents show a very high degree of affinity for Cd.

(b). Soil removes more Cu^{2+} from solution than Cd^{2+} on a Molar basis.

(c). The influence of pH is variable: although increasing pH above a certain level (c.pH 7) tends to reduce solution M^{2+}, organic matter coming into solution tends to maintain solution metal levels.

(d). Cu is more pH sensitive in terms of its own speciation and surface speciation, whilst Cd appears to be mainly responsive to changes in surface speciation.

(e). The presence of inorganic ligands tends to enhance the mobility of Cd to a greater degree than Cu.

(f). The influence of time is variable, most metal uptake is complete within 24 hours.

(g). The CEC is of importance in Cd uptake, and will be much influenced by the amount of organic matter in the soil.

(h). Manganese oxides and iron oxides and organic matter play a major role in Cu uptake on to soil, mainly in a non-exchangeable form.

(i). Few cations,except where in great excess, seem able to influence Cu uptake on to soils.

(j). Zn is able to compete with Cd for uptake, when it is present in relative excess.

Thus, a certain degree of variability in the physico-

chemical determinants of the levels of Cu and Cd which will be found in soils and their solutions can be discerned.

Concern has been expressed in many quarters concerning the disposal of industrial wastes on land, particularly with respect to the levels of potentially phyto- and mammal-toxic metals. However, Jarvis and Jones (1980) have pointed out that the ploughing in of a waste material which had a seemingly high level of Cd associated with it still only brought the soil up to μM levels of Cd. If waste materials are to be used on land which is of agricultural or civic amenity value, or if the metals inputs simply represent the airborne detritus of the industrial age, it would appear to be of importance that the major influences upon the fate of anthropogenic Cu and Cd at the μM levels can be identified, and it is the aim of this project to examine certain aspects of the soil chemistry of copper and cadmium, to assess the potential impact of low level increases in the native soil contents of these metals.

Chapter 2. Characterization of Soils and Analytical Techniques.

The purpose of this chapter is the description of some of the basic features of the soils which were used in this study, to provide a data baseline and highlight any facets of the soils which may serve to explain whatever differences in their behaviour towards copper and cadmium which may be encountered.

2.1. Determination of Soil Properties.

2.1.1. Materials and Methods.

The methods utilized in this section are standard methods outlined in Page *et al* (1982) and MAFF (1986).

The following properties of all eight soils in this project were determined;

(a). Gravimetric moisture content.

10.00g of weighed fresh or air dried soil were dried for 16h, in a porcelain basin, at 110 °C, allowed to cool in a desiccator and reweighed.

$$\text{Moisture content} = \frac{\text{(fresh or air dry weight - oven dry weight)}}{\text{fresh or air dry weight}}$$

(b). Moisture characteristic curve.

Air dried, 2mm sieved, soil samples were equilibrated at various pressures (strictly 'suctions') from 0-1500 kPa using Haines apparatus and a pressure plate. Samples at equilibrium (48h) were collected, weighed, and then dried at

110°C before being reweighed. Moisture contents were calculated on a fresh weight basis and plotted against the applied pressure.

(c). Particle size distribution.

For this, the pipette method (MAFF 1986) was followed.

(d). Organic matter content

1. Loss on ignition (L.O.I.).

The gravimetric determination of organic matter (O.M.) was achieved by ashing, in a muffle furnace, 5.00g of air dried, 2mm sieved, soil in silica basins at 550°C for 5h.

2. Tinsley (Dichromate oxidation).

The chemical determination of organic matter followed the MAFF (1986) method, using 0.25g of air dry, 2mm sieved, soil.

(e). pH.

1. H_2O.

10g of 2mm sieved air dry soil were suspended in 25mls. of distilled H_2O and shaken for 30min. The pH of the stirred suspensions were determined using a combination electrode.

2. 0.02M $CaCl_2$.

The above procedure was repeated, substituting 25mls. of 0.02M $CaCl_2$ for the distilled water.

(f). Cation Exchange Capacity.

Cation Exchange Capacity (CEC) was determined by saturating a 1:4 mixture of 2mm sieved air dry soil:acid washed sand in a glass leaching column with 250mls. of 1M

CH_3COOK at pH7. Excess K^+ was removed by leaching the column with 250mls. of Ethanol. Subsequently, the column was leached with 250mls. of 1M CH_3COONH_4 (pH7) and the displaced K^+ determined by flame photometry.

CEC is expressed as meq/100g (meq = milliequivalents) of air dry soil, where the amount of K^+ removed is a measure of the number of negatively charged soil groups.

(g). Percentage Base Saturation.

This property was determined by leaching a 1:4 air dry 2mm sieved soil:acid washed sand column with 250mls. of 1M NH_4CH_3COO at pH7. Na and K were determined by flame photometry whilst Ca and Mg were quantified by Atomic Absorption Spectrophotometry.

$$\%\text{Base Saturation} = \frac{\Sigma(Na + K + Ca + Mg) \times 100}{CEC}$$

(h). Extractable trace elements.

In these determinations, individual extractions of 2mm sieved air dry soil using the following extractants were performed;

1. 0.05M CaCl2.
2. 0.5M CH_3COOH.
3. 0.05M Ammonium Ethylenediaminetetracetic Acid ($(NH_4)_4EDTA$) at pH7.
4. Tamm's Acid Oxalate (0.18M $(NH_4)_2C_2O_4$ and 0.1M $H_2C_2O_4$)

The soil:solution ratio for 1 and 2 were 1:10, whilst for 3 and 4, 1:50 were used. The suspensions were shaken for 60min. and all determinations were conducted, on the filtrate, by AAS (Atomic Absorption Spectrophotometry).

(i). 0.1M $NaNO_3$ extractable organic matter.

2g of 2mm sieved air dry soil were extracted with 50mls. of 0.1M NaNO3 on an end-over shaker for 24h, and the organic content of the filtrates determined by the above mentioned Tinsley method, the volume of water added prior to the titration step being reduced by the amount of filtrate used (all of the filtrate was used in these determinations).

(j). Soil solution extract composition.

Fresh soils were centrifuged at 2800g for 20min. using Genklene (1,1,1 Trichloroethane), as an immiscible displacent, at a ratio of 1:1 (w/v). Solutions were collected by pasteur pipette and filtered through a 0.45µm membrane filter. Following this, the solutions were analysed for;

K,Na - Atomic Emission Spectrophotometry (AES).

Ca, Mg, Cu, Fe, Al, Cd, Pb, Zn - AAS.

SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^- - High Pressure Liquid Chromatography (HPLC).

pH and conductivity were also measured.

The yield of soil solution was calculated on a gravimetric basis.

2.1.2. Results and Discussion.

Table 2.1. outlines the basic soil characteristics, whilst tables 2.2. (a-d) list the various levels of extractable elements.

Table 2.1. Soil Characteristics.

soil	air=> oven cf.	%Sand	%Silt	%Clay	%O.M. (l.o.i)	%O.M. (Tinsley)	O.M. (mg's)*	pH (H_2O)	pH ($CaCl_2$)	CEC (meq/100g)	% Base saturation
Arkleston	0.907	56.0	14.6	18.4	8.0	7.4	bdl	5.80	5.05	19.9	43.8
Arkleston High Zn	0.941	46.1	26.3	13.7	10.0	11.6	bdl	5.00	4.20	24.4	26.2
Caprington	0.933	47.0	13.8	21.4	17.9	15.0	bdl	5.40	4.70	26.8	57.5
Dunlop	0.834	36.3	29.7	28.9	14.2	12.2	bdl	5.80	5.20	54.8	34.0
Blackstoun Alluvial	0.902	25.4	24.3	28.0	24.0	24.8	0.34	5.30	4.90	62.9	41.4
Dreghorn	0.982	75.3	1.7	17.0	6.0	3.6	bdl	5.80	4.80	17.8	15.0
Fen Arable	0.958	13.2	41.8	29.0	11.3	9.8	1.85	7.40	7.00	55.6	44.3
Fen Subsoil	0.960	11.7	53.8	29.0	7.4	3.2	0.96	8.05	7.50	33.6	97.8

* mg/g of air dry soil in 0.1M $NaNO_3$ extract.

cf = conversion factor.

bdl = below detection limits.

Table 2.2. (a). Soil Extractable Trace Elements; 0.05M $CaCl_2$

Soil	Al	Cd	Cu	Fe	Ni	Pb	Zn
Arkleston	0.69	bdl	7.40×10^{-3}	bdl	2.16×10^{-2}	bdl	0.14
Arkleston High Zn	1.19	2.49×10^{-3}	3.78×10^{-3}	bdl	3.32×10^{-2}	4.83×10^{-3}	0.49
Caprington	0.20	3.56×10^{-4}	7.87×10^{-5}	bdl	2.95×10^{-3}	bdl	0.08
Dunlop	0.58	8.00×10^{-4}	bdl	bdl	4.10×10^{-2}	bdl	0.02
Blackstoun Alluvial	0.30	4.45×10^{-4}	bdl	bdl	3.10×10^{-3}	bdl	0.19
Dreghorn	0.76	bdl	1.20×10^{-2}	1.83×10^{-2}	4.43×10^{-3}	bdl	0.04
Fen Arable	bdl	bdl	2.01×10^{-2}	bdl	bdl	bdl	bdl
Fen Subsoil	bdl	bdl	1.23×10^{-2}	bdl	bdl	bdl	bdl

all figures are µmoles/g oven dry soil.

Notes; as a guide, the detection limits, based on an absorbance of 0.005 units and a soil:solution ratio of 1:25 (average oven dry soil weight of 1.70g) are; Cu - 6.9×10^{-4} µmoles/g, Cd - 15.7×10^{-6} µmoles/g.

(bdl = below detection limits).

Table 2.2. (b). Soil Extractable Trace Elements: 0.5M CH_3COOH.

Soil	Al	Cd	Cu	Fe	Ni	Pb	Zn
Arkleston	9.06	1.07×10^{-3}	0.02	0.29	0.02	9.51×10^{-3}	0.27
Arkleston High Zn	4.93	2.85×10^{-3}	0.18	0.33	0.03	7.98×10^{-2}	0.93
Caprington	2.37	8.89×10^{-5}	6.92×10^{-3}	0.23	2.90×10^{-3}	6.30×10^{-4}	0.03
Dunlop	9.42	4.45×10^{-5}	7.55×10^{-3}	0.23	4.43×10^{-3}	4.80×10^{-4}	0.03
Blackstoun Alluvial	9.52	1.16×10^{-3}	0.01	0.50	0.02	7.05×10^{-3}	0.34
Dreghorn	5.37	1.80×10^{-4}	0.02	0.07	0.01	5.30×10^{-4}	0.05
Fen Arable	1.16	1.85×10^{-5}	0.01	0.22	0.01	1.90×10^{-4}	0.01
Fen Subsoil	0.77	bdl	8.18×10^{-3}	0.18	0.01	3.90×10^{-4}	0.01

all figures are µmoles/g oven dry soil.

Notes; as a guide, the detection limits, based on an absorbance of 0.005 units and a soil:solution ratio of 1:25 (average oven dry soil weight of 1.70g) are; Cu - 6.9×10^{-4} µmoles/g, Cd - 15.7×10^{-6} µmoles/g.

(bdl = below detection limits).

Table 2.2. (c). Soil Extractable Trace Elements: 0.05M NH_4EDTA, pH 7.0

Soil	Al	Cd	Cu	Fe	Ni	Pb	Zn
Arkleston	18.90	4.45×10^{-4}	0.17	8.06	0.07	0.10	0.44
Arkleston High Zn	92.10	5.07×10^{-3}	0.64	9.31	0.06	0.31	1.16
Caprington	11.30	5.34×10^{-4}	0.12	16.85	0.02	0.04	0.04
Dunlop	36.09	5.16×10^{-2}	0.02	4.53	0.01	8.68×10^{-3}	0.11
Blackstoun Alluvial	75.37	3.20×10^{-2}	0.49	41.15	0.14	0.19	0.65
Dreghorn	10.87	bdl	0.12	2.46	0.02	7.20×10^{-4}	0.05
Fen Arable	5.11	bdl	0.12	21.63	0.11	2.03×10^{-3}	0.12
Fen Subsoil	7.02	bdl	0.16	11.14	0.18	2.40×10^{-4}	0.03

all figures are µmoles/g oven dry soil.

Notes; as a guide, the detection limits, based on an absorbance of 0.005 units and a soil:solution ratio of 1:25 (average oven dry soil weight of 1.70g) are; Cu - 6.9×10^{-4} µmoles/g, Cd - 15.7×10^{-6} µmoles/g.

(bdl = below detection limits).

Table 2.2. (d). Soil Extractable Trace Elements: Tamm's Acid Oxalate (pH 3.25).

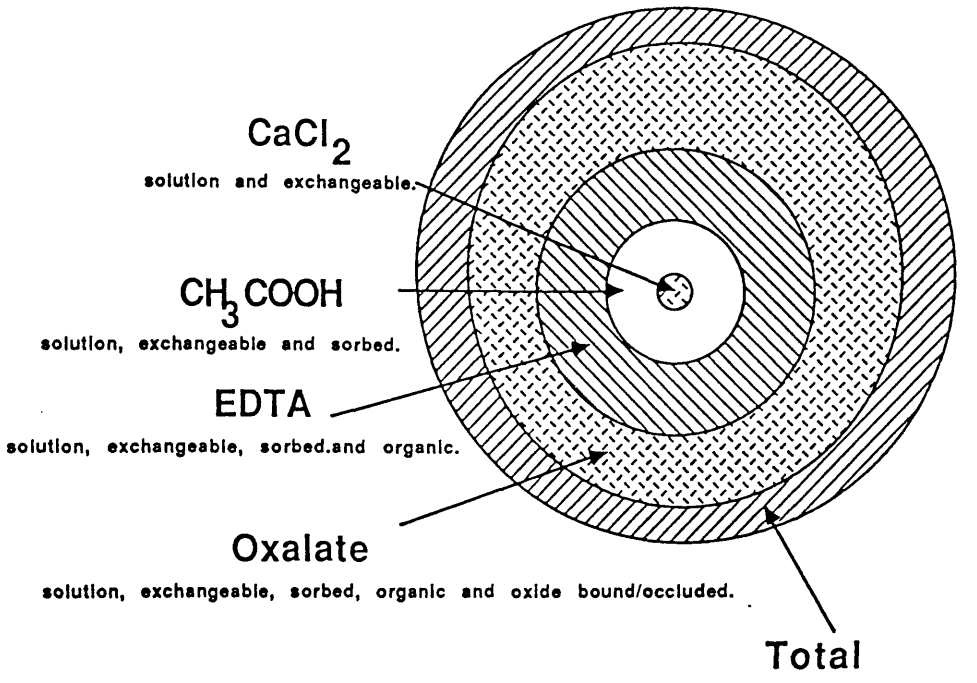
Soil	Al	Cd	Cu	Fe	Ni	Pb	Zn
Arkleston	57.23	3.38×10^{-3}	0.48	110.92	0.17	0.22	0.71
Arkleston High Zn	56.77	4.54×10^{-3}	1.25	195.43	0.18	0.88	1.89
Caprington	41.78	9.00×10^{-5}	0.20	124.97	0.06	0.05	0.11
Dunlop	194.07	bdl	0.08	236.12	0.10	0.03	0.11
Blackstoun Alluvial	122.72	3.91×10^{-3}	1.06	224.03	0.27	0.16	0.78
Dreghorn	90.22	1.60×10^{-3}	0.08	63.57	0.07	0.05	0.11
Fen Arable	21.02	5.30×10^{-4}	0.08	102.48	0.22	0.02	0.15
Fen Subsoil	16.28	2.00×10^{-5}	0.04	39.86	0.18	2.51×10^{-3}	0.06

all figures are µmoles/g oven dry soil.

Notes; as a guide, the detection limits, based on an absorbance of 0.005 units and a soil:solution ratio of 1:25 (average oven dry soil weight of 1.70g) are; Cu - 6.9×10^{-4} µmoles/g, Cd - 15.7×10^{-6} µmoles/g.

(bdl = below detection limits).

In most of the soils (5 out of 8), oxalate extracted the greatest amount of Cu, which is what would be expected, given the following suppositions regarding the nature of the attack of the extractants on the pools of metal in the soils (see diagram below).



Systematic division of nutrient 'pools' in soil.

For Cd the EDTA and oxalate removed the greatest amount . In most cases, the solution and exchangeable forms of Cu and Cd are insignificant, except with the Fen soils, where Ca^{2+} displaced more Cu^{2+} than H^+ (Acetic acid). This may be simply a function of the presence of a calcium-containing mineral (calcite - calcium carbonate) in the system and that the ionic size and solubility product considerations become dominant.

Generalities which may be drawn from this data are:

(a). Exchangeable and solution forms of Cu and Cd were insignificant.

(b). Quantitatively, most Cu is present in the oxide fraction.

(c). EDTA extracts imply that organic matter was an important source of soil Cd, except in the Fen soils, where co-precipitation or occlusion of (effectively) $CdCO_3$ may occur: hence, acid dissolution of these phases led to release of Cd.

Soil solution extracts were obtained by immiscible displacement centrifugation, using 1,1,1 Trichloroethane as the displacing solvent. The yield of solution, using a 1:1 ratio of fresh soil to solvent was as follows;

Arkleston	11% of total H_2O
Arkleston High Zinc	25% total H_2O
Dunlop	24% total H_2O
Blackstoun Alluvial	14% total H_2O

Given the equipment available on which to perform the extractions (20 minutes at a maximum of 2800g) these were the only four soils from which solution could be obtained. The chemical analysis of these solutions is presented in table 2.3., and the moisture characteristic curves for all eight soils in fig. 2.1. (a-h).

Table 2.3. 1,1,1 Trichloroethane soil solution extracts.

Soil	pH	Conductivity (mS)	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}	Pb^{2+}	Fe^{3+}	Al^{3+}
Arkleston	5.58	1.2	478.5	409.2	1836.7	58.6	0.2	bdl	0.5	0.003	7.2	21.5
Arkleston High Zn	3.94	1.8	1109.2	1662.4	1754	71.6	1.1	26.8*	197.0	244.7	15.7	53.6
Dunlop	4.08	0.4	348.0	76.7	155.9	15.5	2.4	bdl	0.6	bdl	7.9	34.6
Blackstoun Alluvial	4.50	0.8	326.2	639.4	1625.6	26.4	0.2	bdl	0.9	0.002	19.1	52.6

soil	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	anions/cations	pores emptied#
Arkleston	1.0§	10.0§	1.3§	bdl	4.4	>2.4µm
Arkleston High Zn	0.7§	12.3§	4.0§	bdl	3.5	>0.7µm
Dunlop	1.1§	4.0§	0.9§	bdl	9.4	>0.2µm
Blackstoun Alluvial	1.6§	8.6§	1.3§	bdl	4.3	>1.9µm

(bdl = below detection limits).

all figures are µM, except where indicated; * - nM, § - mM.

#obtained via the expression d=-4Y/ç: Where d is the equivalent cylindrical diameter of the pore, Y is the surface tension of H_2O at 25 °C (0.07197 N/m), and ç is the negative pressure read from the moisture characteristic curve for the given water content, post centrifugation.

Figure 2.1. (a-h).

Moisture characteristic curves for the soils used;

(a). Arkleston.

(b). Arkleston High Zinc.

(c). Caprington.

(d). Dunlop.

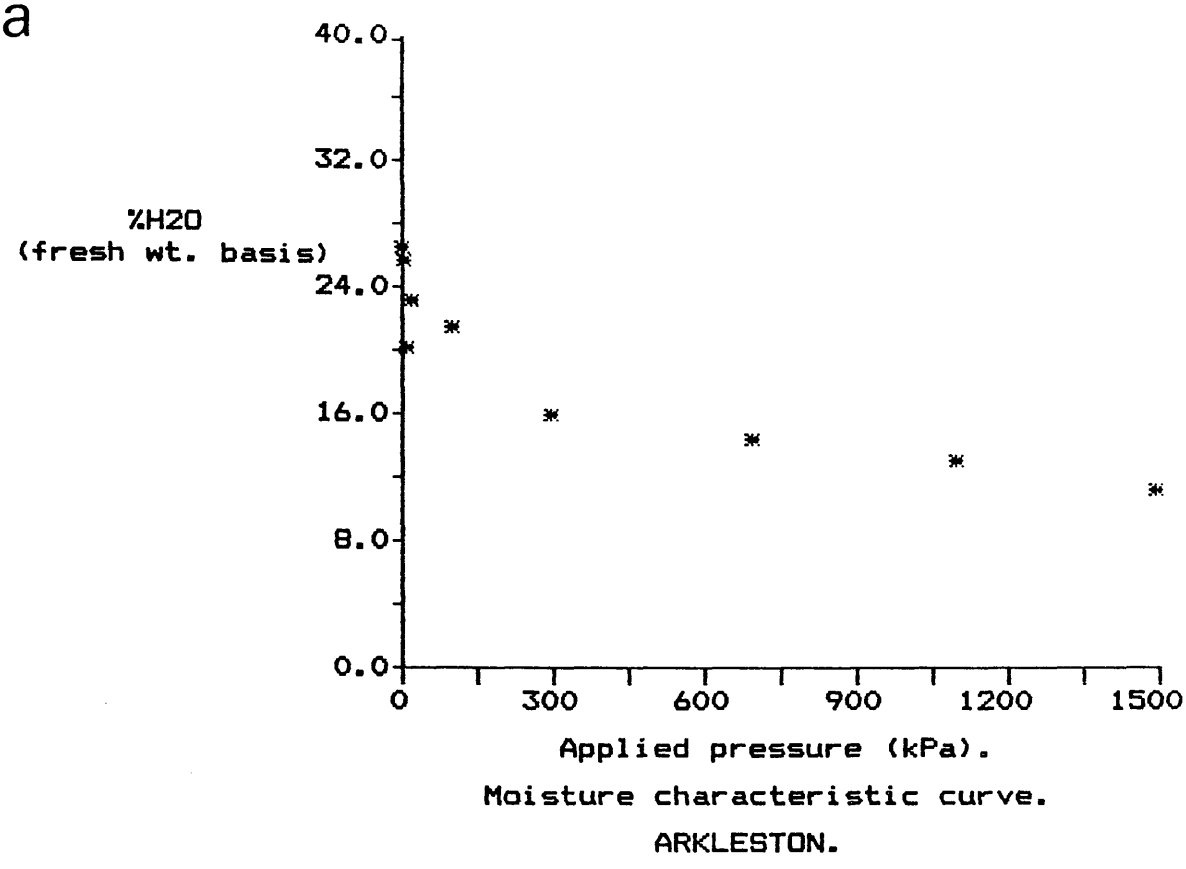
(e). Blackstoun Alluvial.

(f). Dreghorn.

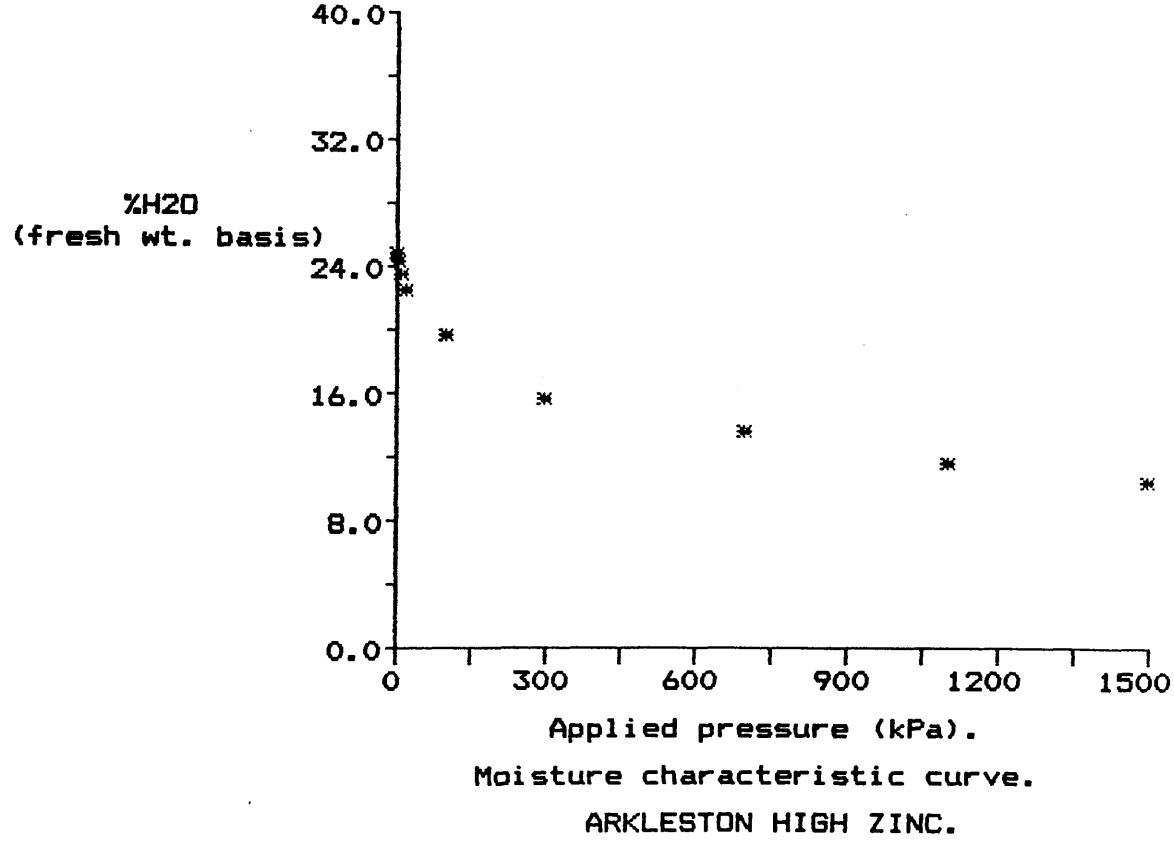
(g). Fen Arable.

(h). Fen Subsoil.

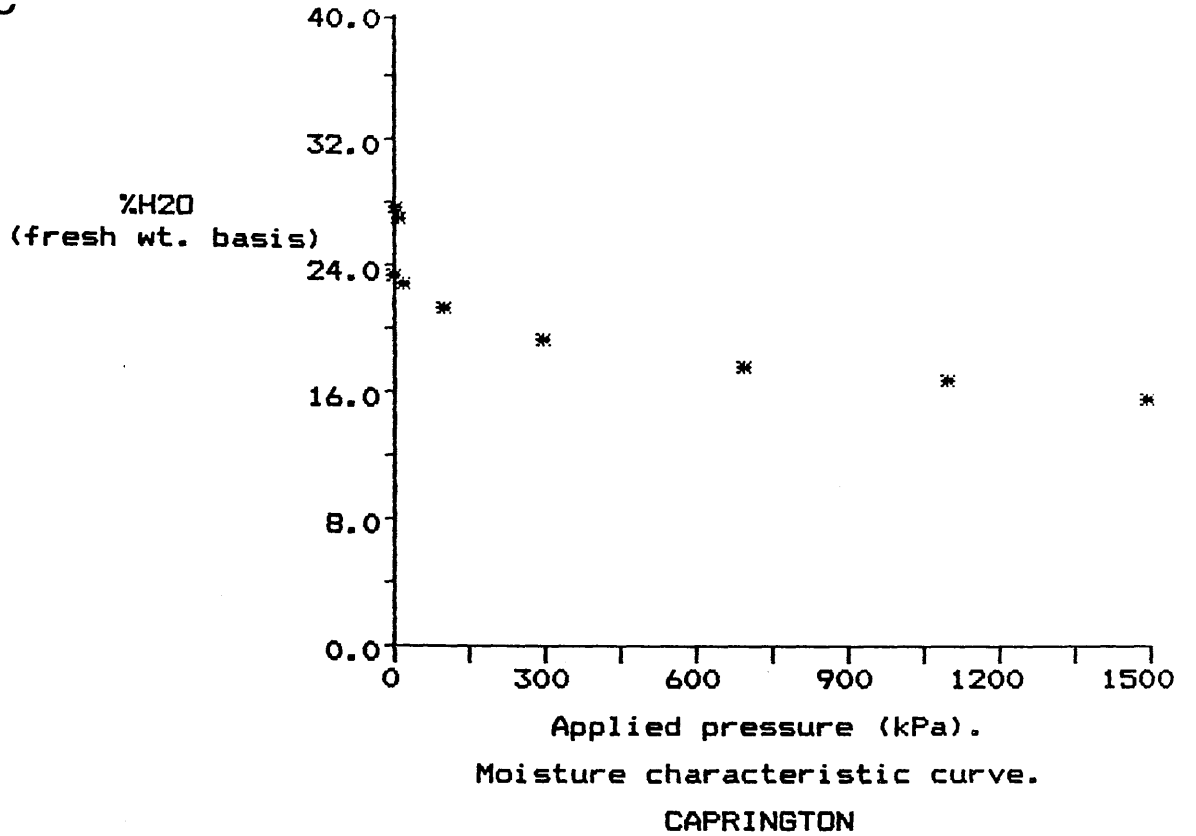
a


%H2O
(fresh wt. basis)
40.0
32.0
24.0
16.0
8.0
0.0
0
300
600
900
1200
1500
Applied pressure (kPa).
Moisture characteristic curve.
ARKLESTON.

b


%H2O
(fresh wt. basis)
40.0
32.0
24.0
16.0
8.0
0.0
0
300
600
900
1200
1500
Applied pressure (kPa).
Moisture characteristic curve.
ARKLESTON HIGH ZINC.

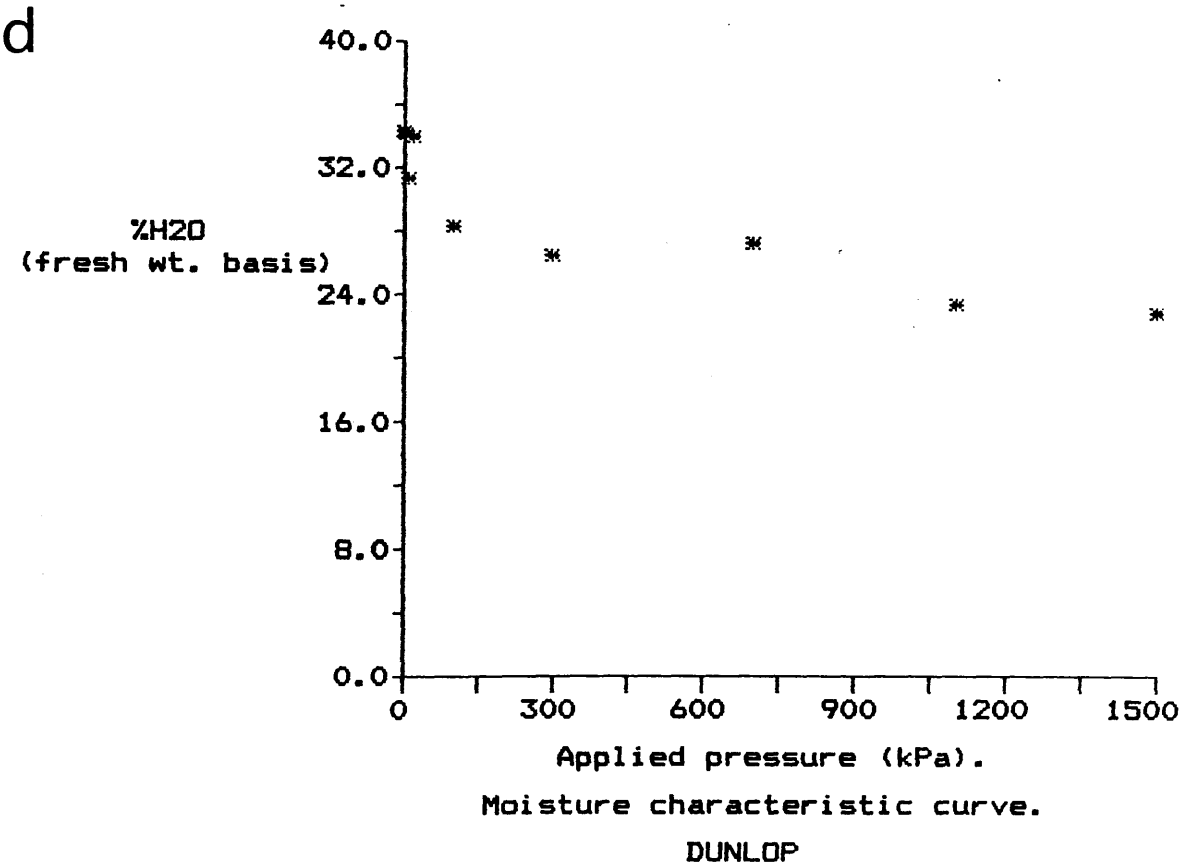
c



Moisture characteristic curve.

CAPRINGTON

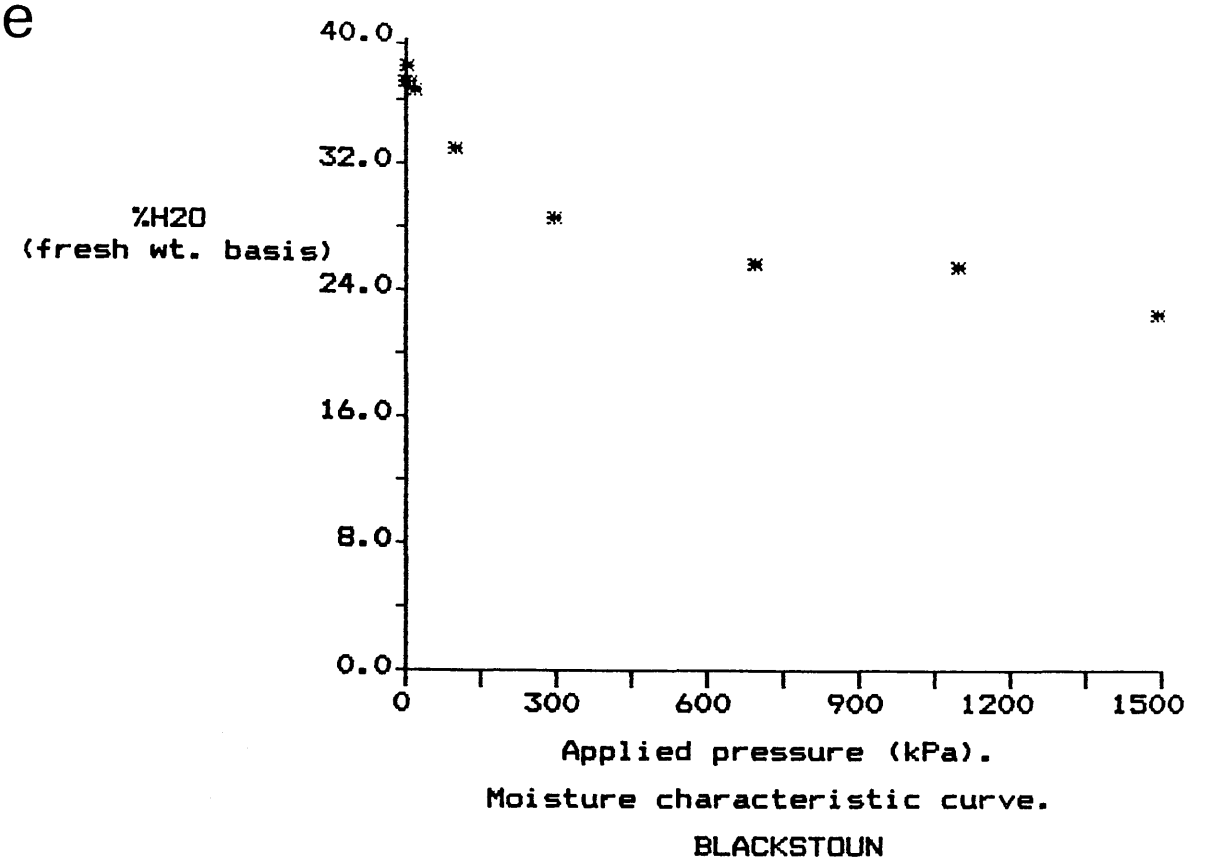
d



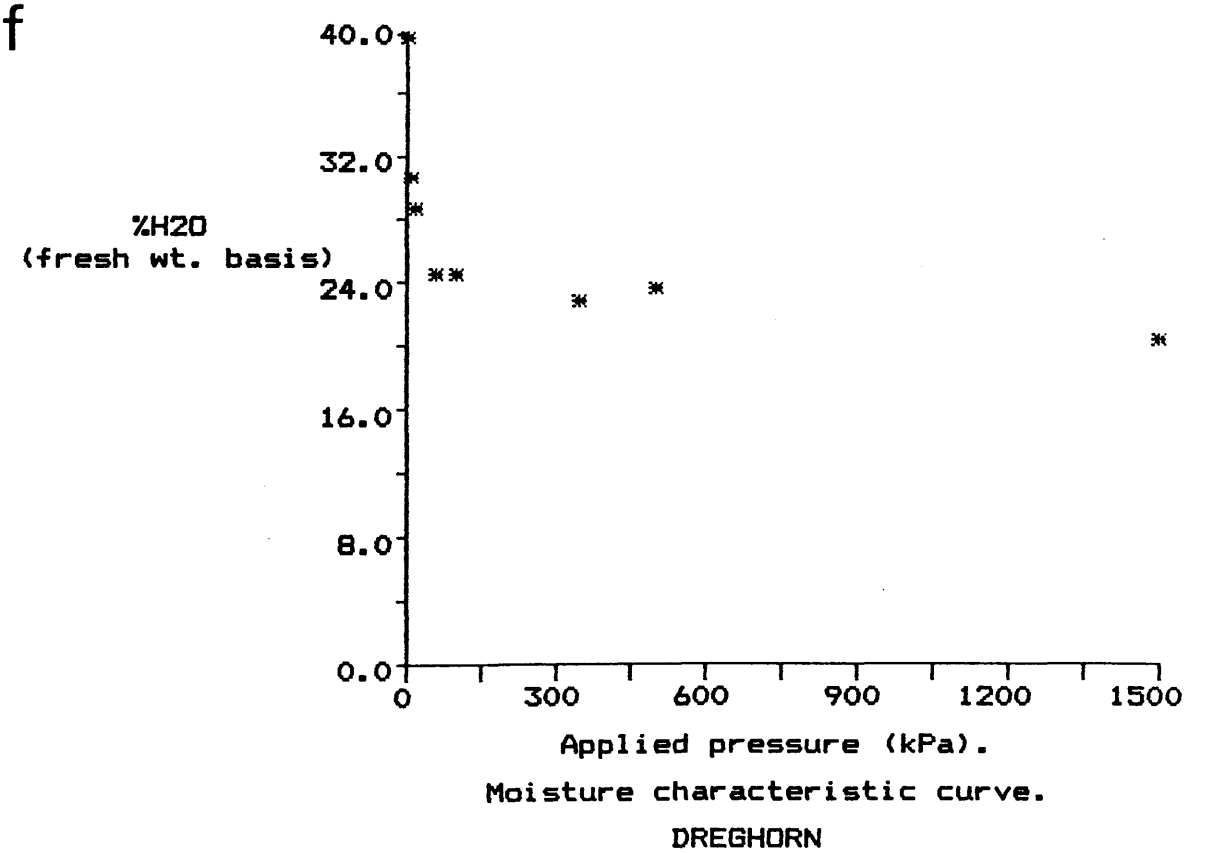
Moisture characteristic curve.

DUNLOP

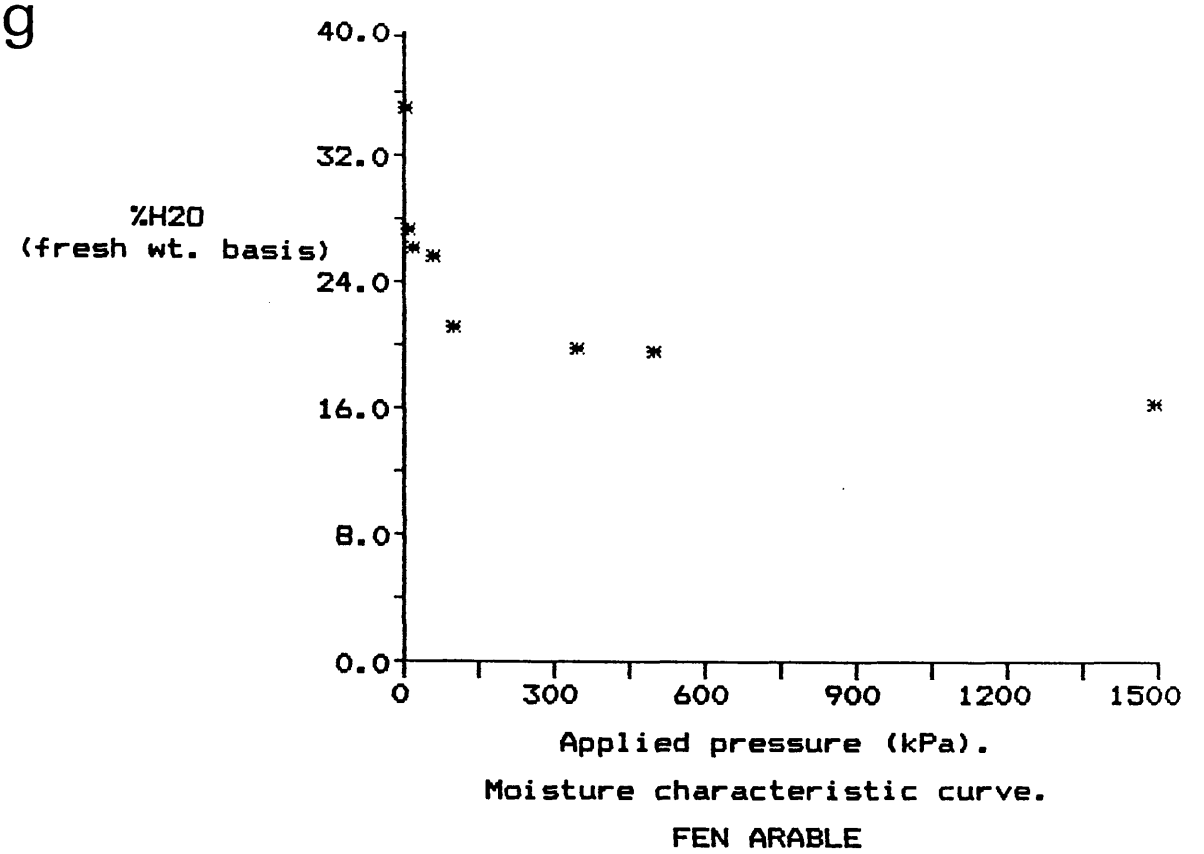
e


40.0
32.0
24.0
16.0
8.0
0.0
%H2O
(fresh wt. basis)
0
300
600
900
1200
1500
Applied pressure (kPa).
Moisture characteristic curve.
BLACKSTOUN

f


40.0
32.0
24.0
16.0
8.0
0.0
%H2O
(fresh wt. basis)
0
300
600
900
1200
1500
Applied pressure (kPa).
Moisture characteristic curve.
DREGHORN

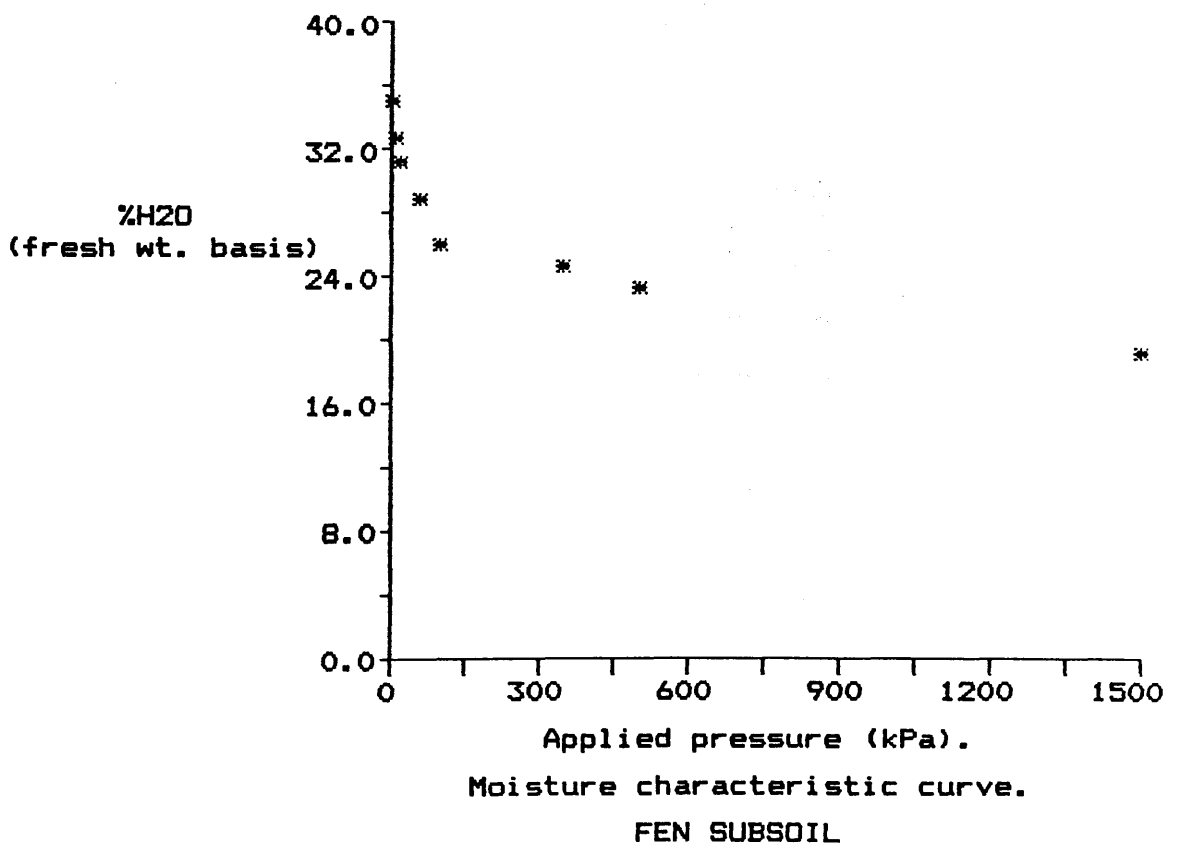
g



Moisture characteristic curve.

FEN ARABLE

h



Moisture characteristic curve.

FEN SUBSOIL

According to Griffin and Jurinak (1973), the ionic strength of solutions can be estimated from their electrical conductivities. Several authors have pursued this line of thought and there is a remarkable degree of agreement in their findings; where EC (Electrical Conductivity) is measured in mS (milli-Siemens),

Equation.	Reference.
I=0.013EC	Griffin and Jurinak (1973).
I=0.012EC - 0.0004	Gillman and Bell (1978).
I=0.014EC - 0.0002	Black and Campbell (1982).
I=0.01162EC - 0.000105	Pasricha (1987).
I=0.011EC - 0.0008	Menzies and Bell (1988).
I=0.010EC - 0.0005	*ibid.*

This gives an 'average' equation of;

$$I=0.012EC - 0.0003$$

and from this we can estimate I for the extracted solutions.

Arkleston	I=0.0141M.
Arkleston High Zinc	I=0.0213M.
Dunlop	I=0.0045M.
Blackstoun Alluvial	I=0.0093M.

Most authors have found a reasonable degree of agreement between the sum of the cations and anions in solutions obtained by centrifugal soil extraction. With the solutions obtained in this study, the anion levels are of the order of magnitude indicated by the ionic strength predictions, however the cation levels were very much lower than the anions. Any discrepancy between the two figures would be expected to show higher levels of cations

than anions, as the organic component of the solution was not accounted for. The approaches used by other authors have allowed them to obtain much higher volumes of soil solutions. Edmeades *et al* (1985) used air displacement and recovered 30-60% of the soil solution, whilst Kinniburgh and Miles (1983) used a Fluorocarbon immiscible displacing solution, but with a very high powered centrifuge (13-20,000g). These approaches, possibly, give a much more representative sample of the soil water. Clearly there is a need to be able to determine a wider range of solution components if any degree of parity is to be found between the anion and cation levels.

2.2. Analytical Methodology.

In the investigations into the nature of the soil - solution interactions of Cu and Cd, several analytical methods were employed. The main method of metal quantification was AAS, (Atomic Absorption Spectrophotometry), both in its flame and furnace modes.

A further means of metal analysis which was investigated was the Ion-Selective Electrode (ISE), whilst when looking at anion levels, single column indirect U.V spectrophotometric High Pressure Piquid Chromatography (HPLC) was used.

2.2.1. Atomic Absorption Spectrophotometry

The instruments used for flame analysis were all made by **Perkin-Elmer**, the models being 306, 370A and 1100B: where flame analyses were carried out, 'cookbook' settings and standard linear ranges were applied.

Graphite furnace AAS (GFAAS) work was performed

initially on the 306 instrument, using the HGA-74 furnace and manual 10-20 µL injections. The 1100B, and the AS-70 autosampler were used in the final stages of this project. Pyrolite coated tubes were always used in furnace work. Standards, which were usually multi-element, were matrix matched with the samples. Below are tabulated the working conditions found for the flame and furnace systems. (tables 2.4-7.).

Table 2.4. Detection limits and dilution recommendations for Flame AAS.

Table 2.5. Linear calibration ranges for Furnace AAS.

Table 2.6. Temperature parameters for GFAAS using the HGA-74.

Table 2.7. Temperature parameters for GFAAS using the 1100B.

tab.2.4.

Flame AAS detection limits (based on app. 0.005 absorption):

Aluminium: 1.14 ppm (42.2uM).at detection limit,dilute 1:10 for furnace use.

Cadmium: 0.03 ppm (0.27 uM).at detection limit,dilute 1:10 for furnace use.

Copper: 0.10 ppm (1.56 uM).at detection limit,no dilution needed for furnace use.

Iron: 0.14 ppm (2.51 uM).at detection limit,dilute 1:5 for furnace use.

Manganese: 0.06 ppm (1.09 uM) at detection limit,dilute 1:5 for furnace use.

Nickel: 0.17 ppm (2.90 uM).at detection limit,no dilution needed for furnace use.

Lead: 0.56 ppm (2.70 uM).at detection limit,dilute 1:10 for furnace use.

Zinc: 0.02 ppm (0.30 uM).at detection limit,dilute 1:10 for furnace use.

tab.2.5.

Furnace Atomic Absorption linear calibration ranges.
Aluminium: 0.0 - 200.0 ppb. (0.0 -7.4 uM).

Cadmium: 0.0 - 7.5 ppb.(0.0 - 66.7 nM).

Copper: 0.0 - 150.0 ppb.(0.0 - 2.4 uM).

Iron: 0.0 - 75.0 ppb.(0.0 - 1.3 uM).

Manganese: 0.0 - 30.0 ppb.(0.0 - 550.0 nM).

Nickel: 0.0 - 350.0 ppb.(0.0 - 6.0 uM).

Lead: 0.0 - 125.0 ppb.(0.0 - 600.0 nM).

Zinc: 0.0 - 6.0 ppb.(0.0 - 92.0 nM).

Based on 10 uL injections.
PE 306 + HGA 74 : recorder - 2 mV FSD.
- 5 mm/min.

Table 2.6. HGA-74 Conditions.

All the numerical settings refer to the digits on the console and not directly to the temperatures and times are in seconds.

(injection volume = 20µL, Pyrolite coated tubes used).

All times are in seconds.

	Drying 1		Drying 2		Ramp Ashing		Atomisation		Clean-up	
Element	setting	time	setting	time	rate	setting	setting	time	setting	time
Aluminium	65	20	69	20	8	500	999	10	999	10
Cadmium	60	20	66	20	8	140	250	7	999	5
Copper	60	20	65	20	7	350	900	8	999	5
Iron	60	20	65	20	4	350	990	8	999	5
Lead	65	20	69	20	7	280	940	7	999	5
Manganese	65	20	75	20	8	390	990	8	999	5
Nickel	65	20	69	20	9	450	800	8	999	5
Zinc	60	20	65	20	7	150	300	8	999	6

Element: FE Wavelength: 248.3 nm Slit: 0.2 L

Step Number	Furnace Temperature	Time Ramp	Time Hold	Internal Gas Flow	Read On	Repeat
1	70	10	1	300		-
2	400	25	5	300		-
3	1100	5	10	300		-
4	2000	0	3	0	0.0	-
5	2650	1	3	300		-
6		1	1	300		-
7		1	1	300		-
8		1	1	300		-
9		1	1	300		-

Injection Temperature: °C
HGA: Idle Step of 0 Temp.: °C Time: s A/S Pos: 1

Element: PB Wavelength: 283.2 nm Slit: 0.7 L

Step Number	Furnace Temperature	Time Ramp	Time Hold	Internal Gas Flow	Read On	Repeat
1	180	20	1	300		-
2	400	15	5	300		-
3	800	15	5	300		-
4	1300	0	5	0	0.0	-
5	2650	1	5	300		-
6		1	1	300		-
7		1	1	300		-
8		1	1	300		-
9		1	1	300		-

Injection Temperature: °C
HGA: Idle Step of 0 Temp.: °C Time: s A/S Pos: 1

Element: ZN Wavelength: 213.9 nm Slit: 0.7 L

Step Number	Furnace Temperature	Time Ramp	Time Hold	Internal Gas Flow	Read On	Repeat
1	180	20	1	300		-
2	320	10	10	300		-
3	1110	0	4	0	0.0	-
4	2650	1	5	300		-
5		1	1	300		-
6		1	1	300		-
7		1	1	300		-
8		1	1	300		-
9		1	1	300		-

Injection Temperature: °C
HGA: Idle Step of 0 Temp.: °C Time: s A/S Pos: 1

tab.2.7.

Element: AL Wavelength: 309.3 nm Slit: 0.7 L

Step Number	Furnace Temperature	Time Ramp	Time Hold	Internal Gas Flow	Read On	Repeat
1	70	10	1	300		-
2	400	25	5	300		-
3	1500	10	1	300		-
4	2400	0	3	0	0.0	-
5	2650	1	3	300		-
6		1	1	300		-
7		1	1	300		-
8		1	1	300		-
9		1	1	300		-

Injection Temperature: °C
HGA: Idle Step of 0 Temp.: °C Time: s A/S Pos: 1

Element: CD Wavelength: 228.6 nm Slit: 0.7 L

Step Number	Furnace Temperature	Time Ramp	Time Hold	Internal Gas Flow	Read On	Repeat
1	70	1	10	300		-
2	150	1	10	300		-
3	500	30	5	300		-
4	1110	0	5	0	0.0	-
5	2650	1	5	300		-
6		1	1	300		-
7		1	1	300		-
8		1	1	300		-
9		1	1	300		-

Injection Temperature: °C
HGA: Idle Step of 0 Temp.: °C Time: s A/S Pos: 1

Element: CU Wavelength: 324.7 nm Slit: 0.7 L

Step Number	Furnace Temperature	Time Ramp	Time Hold	Internal Gas Flow	Read On	Repeat
1	70	10	1	300		-
2	450	30	1	300		-
3	1100	20	5	300		-
4	2000	0	5	0	0.0	-
5	2650	1	3	300		-
6		1	1	300		-
7		1	1	300		-
8		1	1	300		-
9		1	1	300		-

Injection Temperature: °C
HGA: Idle Step of 0 Temp.: °C Time: s A/S Pos: 1

tab.2.7.

The main problem encountered with the GFAAS (Graphite Furnace or Electrothermal AAS) analysis was the matrix absorbance by the background electrolyte most used in this study: 0.1M $NaNO_3$. Most could be charred off at 1300°C, but for less refractory elements, this became impracticable, and, thus, for Cd and Zn, relatively low atomization temperatures were used (c.1100°C). Working with the 1100B allowed D_2-Arc background correction to be routinely used as a check to ensure that the analyte signal was free from interference from the $NaNO_3$.

2.2.2. Ion - Selective Electrodes.

The importance of chemical speciation has already been pointed out (section 1.2.3.), as has been the dearth of any analytical techniques which can unambiguously be applied to the problem. However, if interest lies in the activity of the 'free' ion, then the means to determine it are, for many ions, available in the shape of Ion-Selective Electrodes (ISE's).

The theory behind the use of ISE's is that they respond solely to the 'free' metal ion (for further information *cf.*Bailey (1980) and Kamman (1979)). The copper and cadmium ISE's (**Russell Electrodes**) used here rely upon the sensitivity of a highly insoluble metal Sulphide membrane to changes in the metal ion activity in contact with it to yield emf (electro - motive force) values which can be related to activities.

As explained in section 1.2.3., Cu and Cd speciation is altered by

(a). pH

(b). Ionic strength (I)

(c). The presence of ligands

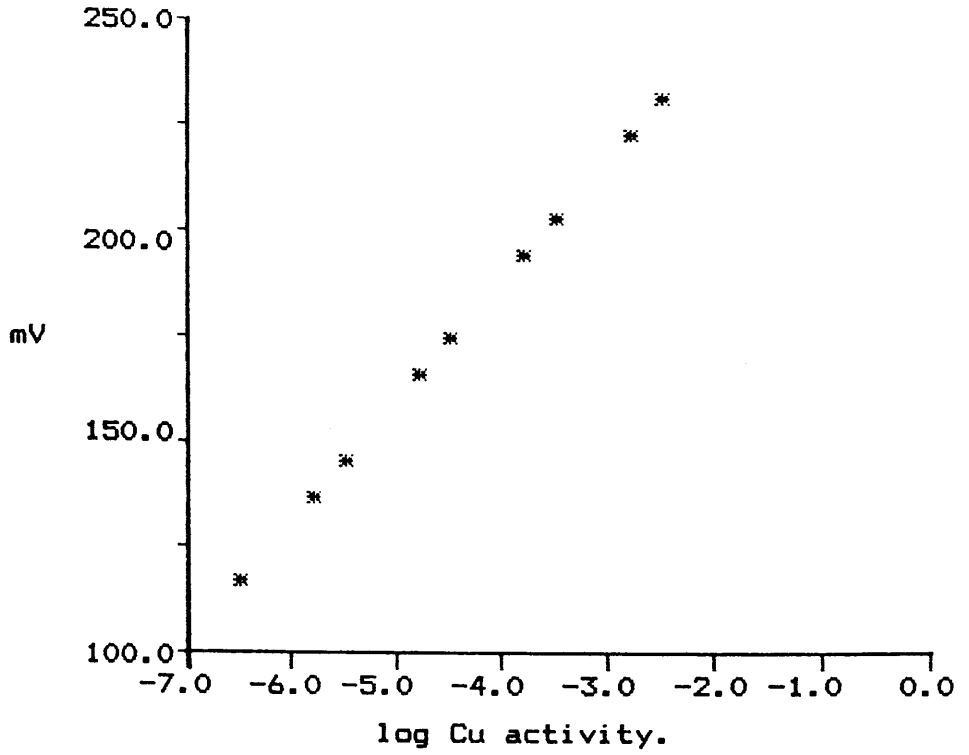
Thus, the emf discerned by the electrochemical cell will vary according to these parameters. However, if a standard system is chosen in which the solution composition, pH and ionic strength are known, the electrode can be calibrated in terms of 'free' metal ion activity, a scale which is independent of pH, I and solution composition. The electrodes were activity calibrated at pH 4.0, I = 0.1M $NaNO_3$ in equilibrium with atmospheric CO_2 ($p \approx 10^{-3.52}$ atm.) and the following calibration graphs were obtained: figs. 2.2. and 2.3., which demonstrated Nernstian response for $(Cu^{2+})_{free} > 10^{-7}M$ and $(Cd^{2+})_{free} > 10^{-6}M$.

Figures 2.2. and 2.3. ISE Calibration Graphs.

(a). Cupric ISE, I=0.1M $NaNO_3$, pCO_2=10-3.52, pH=4.0

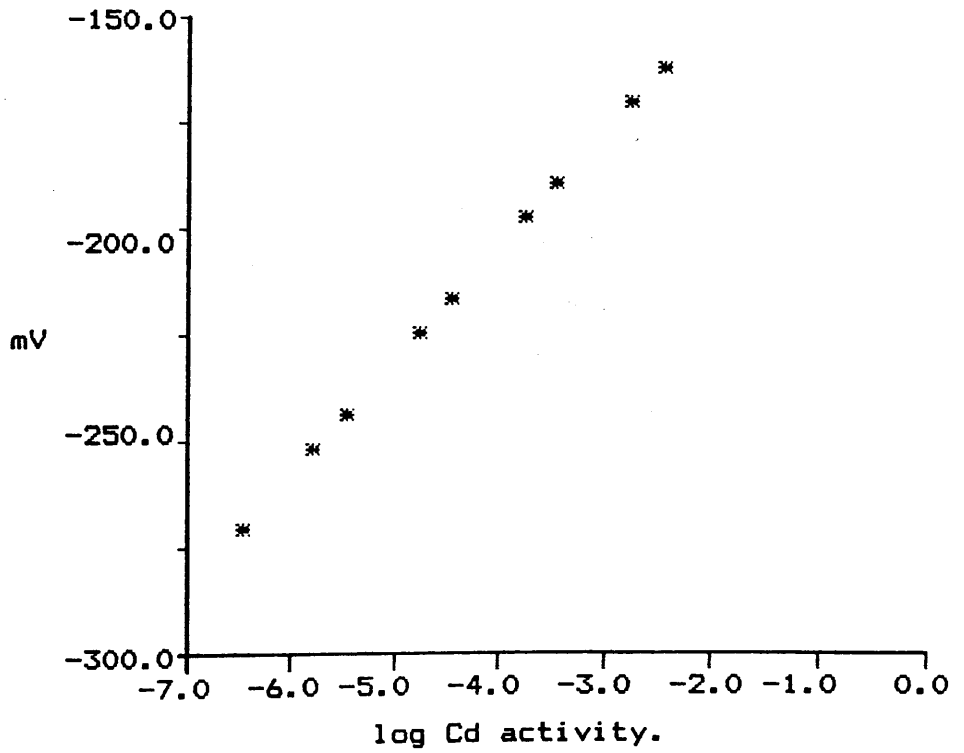
(b). Cadmium ISE, I=0.1M $NaNO_3$, pCO_2=10-3.52, pH=4.0

fig.2.2.



Cu ISE calibration;pH=4,I=0.1M NaNO3,pCO2=10^-3.52.
Ag/AgCl reference electrode.

fig.2.3.



Cd ISE calibration;pH=4,I=0.1M NaNO3,pCO2=10^-3.52.
Ag/AgCl reference electrode.

As the name of these instruments suggests, they are selective, and many interferences are possible. The Cupric ISE is relatively stable and only Ag and S^{2-} interfere to any degree, however, the cadmium ISE is subject to interferences from some common soil cations;

Cu2+	>10-6M	
Ca2+	>0.22mM	personal communication
Mg2+	>0.15mM	from manufacturers.

Cavallaro and McBride (1980b) noted that Al^{3+} interfered with both the Cu and Cd electrodes, which may prove to be a problem when using them in acidic soils.

Amacher (1984) has pointed out some of the drawbacks of employing ISE's in soil studies;

(a). Inability to determine activities at the low levels encountered in soil solutions.

(b). Interferences from other ions.

(c). Drifting of readings, due to clogging of junctions, poisoning of membranes and changes in temperature.

A further point of concern when employing ISE's in soil studies is the influence of pH and the role of the suspension effect. This phenomenon is the result of performing measurements in a system in which there are charge bearing colloids. Whether this is considered to be a Donnan membrane effect (Jenny *et al* 1950), the influence of the E_j (junction potential)(Bailey 1980), or being due to the movement of the reference electrode filling solution (Oman and Godec 1986), the result is a difference in pH between a suspension of soil and its supernatant - figure 2.4.

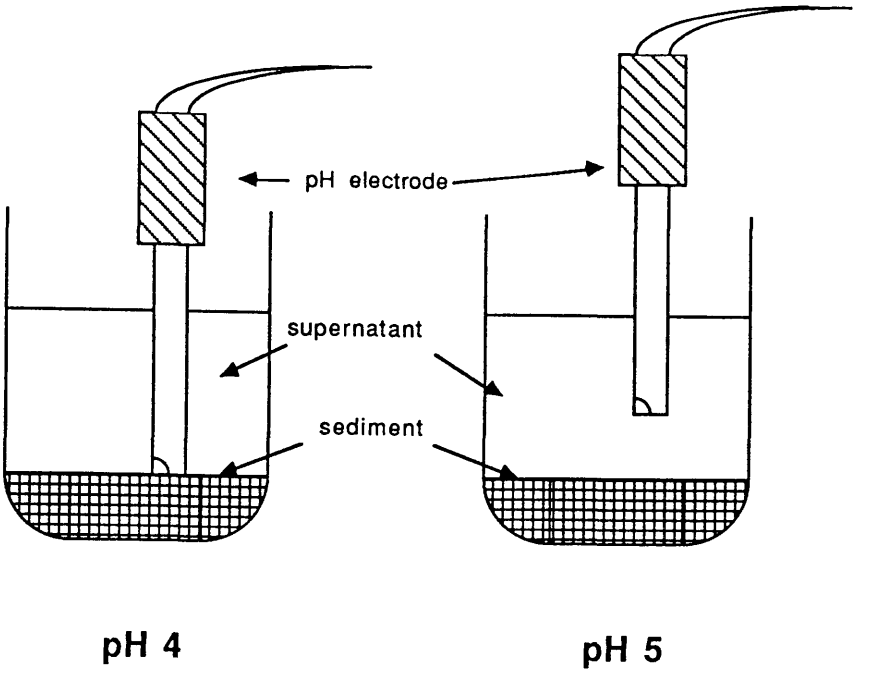


Figure 2.4. The Suspension effect.

As noted above, metal activity is responsive to changes in pH, thus the problem of defining soil pH is mirrored in the attempt to measure soil metal activities - solution or suspension?

A further problematical area in dealing with slurry-based measurements is that of the potential at which the soil suspension exists. In studies of waterlogged soils the E_h, or soil potential, is commonly measured, using a Platinum electrode and a suitable reference electrode. This frequently demonstrates the existence of positive or negative soil potentials of great magnitude (Russell, 1973, p.672, table 25.1) - one can only speculate as to the influence which such high potentials could exert upon other emf-dependent measurement systems (for any M^{2+} electrode, a change in reading of 29mV represents a change in activity of one order of magnitude). The only positive aspect of the suspension effect, as pointed out by Yu (1985), is that it is considered to be due to the junction

potential, then the sign and size of E_j is related to the charge carried by the soil.

Table 2.8. lists the equipment used in making Cu or Cd activity measurements.

Table 2.8. ISE Measuring Equipment.

ISE's	Russell electrodes Cu ISE (94 - 4299).
	Russell electrodes Cd ISE (94 - 4489).
Reference electrode;	
	Russell electrodes Ag/AgCl (90 - 00)
mV meter	Radiometer pH 64 research meter.

notes on operation

(a) All ISE measurements were performed with continuously stirred systems.

(b) The Ag/AgCl reference electrode is sensitive to UV light and is best used in a screened area.

2.2.3. High Pressure Liquid Chromatography.

The determination of inorganic anions in analytical chemistry is a problem. Most procedures are based upon the classical 'wet' chemical determinations of precipitates, colorimetry, turbidimetric or nephelometric processes: either way, they require a sizeable volume of sample and are usually subject to interferences, whilst their sensitivity is usually poor. This lack of sensitivity and the requirement for quite large sample volumes poses a problem for environmental chemists. Whether dealing with rock, sediments or soil, the amount of native solution which can

be extracted from these materials is fairly low compared to the total weight of the material, but, as the soil solution is the closest approach which may be made to the analysis of what happens to solutes in soils, there is a definite need to be able to examine these solutions. Thus HPLC is an attractive option, offering the possibility of multi-ion analysis on a low volume of sample (<0.1mL).

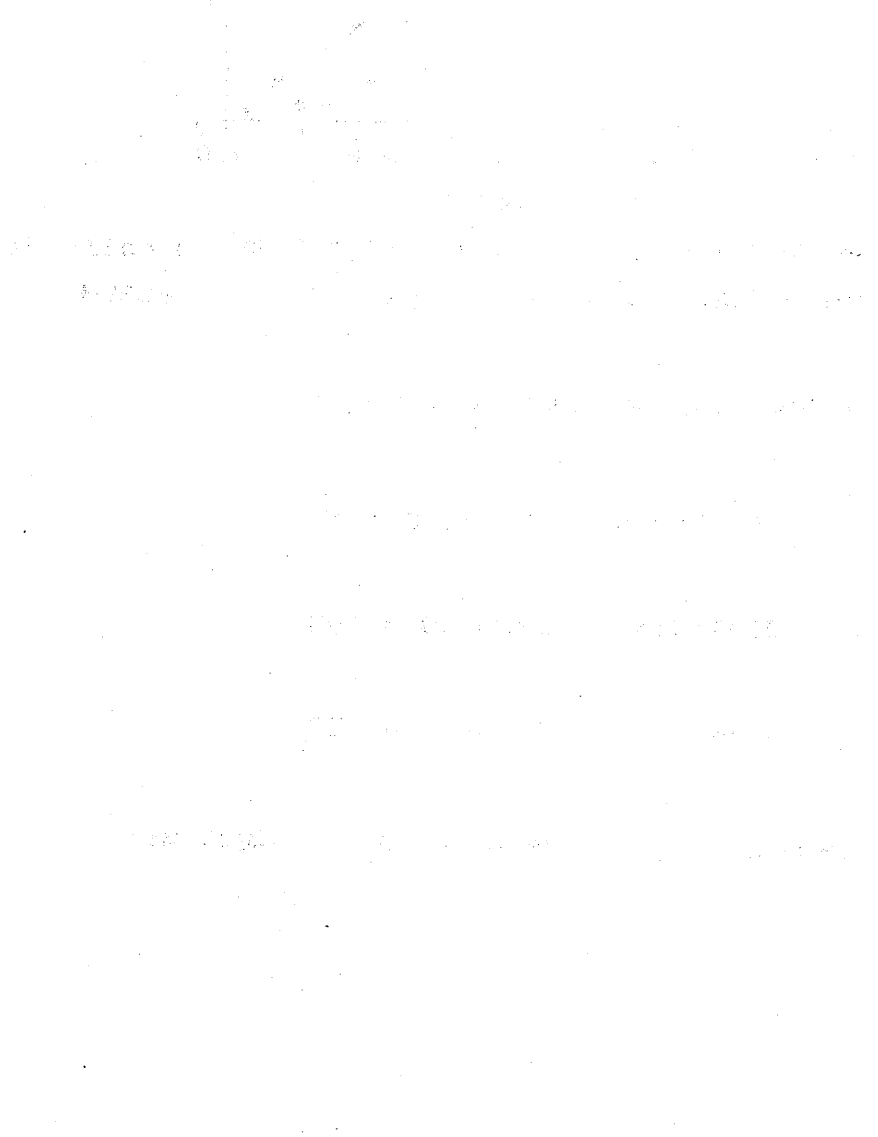
Analysis was limited to a single column system (**Vydac**) with the detection system of indirect UV - absorbance (a series of papers by Nieto and Frankenberger (1985), Karlson and Frankenberger (1986, 1987) and Cape (1987) gives a good idea of the potential of SCIC (Single column ion chromatography) used with a conductivity detector).

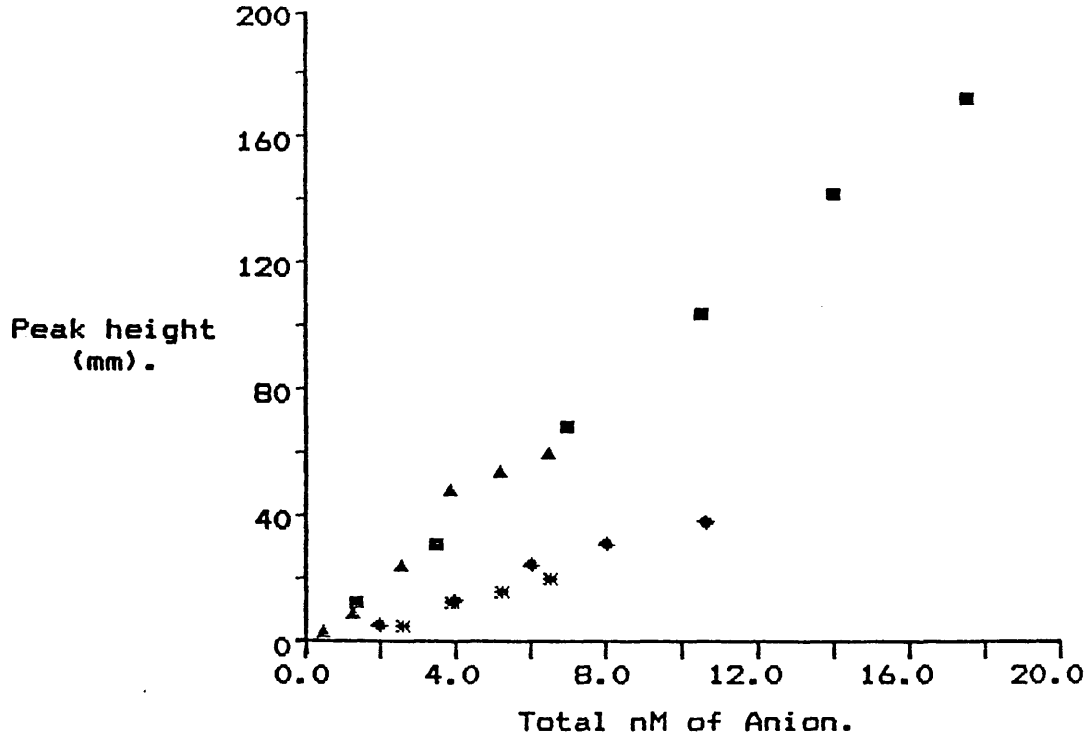
The principle of this system is the use of an ion exchange column, usually a quaternary amine, in alliance with a mobile phase which posesses good UV absorbance characteristics. Thus, with the system fully equilibrated with this mobile phase, a chart recorder's output would show a continuous straight line. The presence of other species in the column eluate represent a depression in the amount of UV absorbing material passing through the detector, and thus the recorder traces a negative 'peak'. This method has been reviewed by Harrison *et al*(1986) and Mullins (1987). The conditions used in this study are as presented in table 2.9., along with a typical calibration graph (figure 2.5.) and recorder trace (figure 2.6.).

Table 2.9. HPLC Conditions and Equipment.

Column - Vydac 302 IC, 25cm.
Perkin Elmer Series 400 Liquid Chromatograph.
Perkin Elmer ISS-100 Autosampler.
Perkin Elmer 56 Chart Recorder.
Solvent; 2mM Potassium Hydrogen Phthalate, pH4.2.
Flow Rate; 1.2mls./min.
Detection Wavelength; 299nm, attenuation 0.02.
Injection Volume; Variable, up to 100µl.
Recorder; 20mV FSD, 5mm/min.
Run Time; 40 min.

Figure 2.5. A Typical Anion HPLC Calibration Graph.





Calibration of HPLC Anion exchange system (IUV detection).

H2PO4 - * Cl - sq. NO3 - dia. SO4 - tri.

$$H2PO4 = 1.12438 + 0.26269 * pk.ht.$$

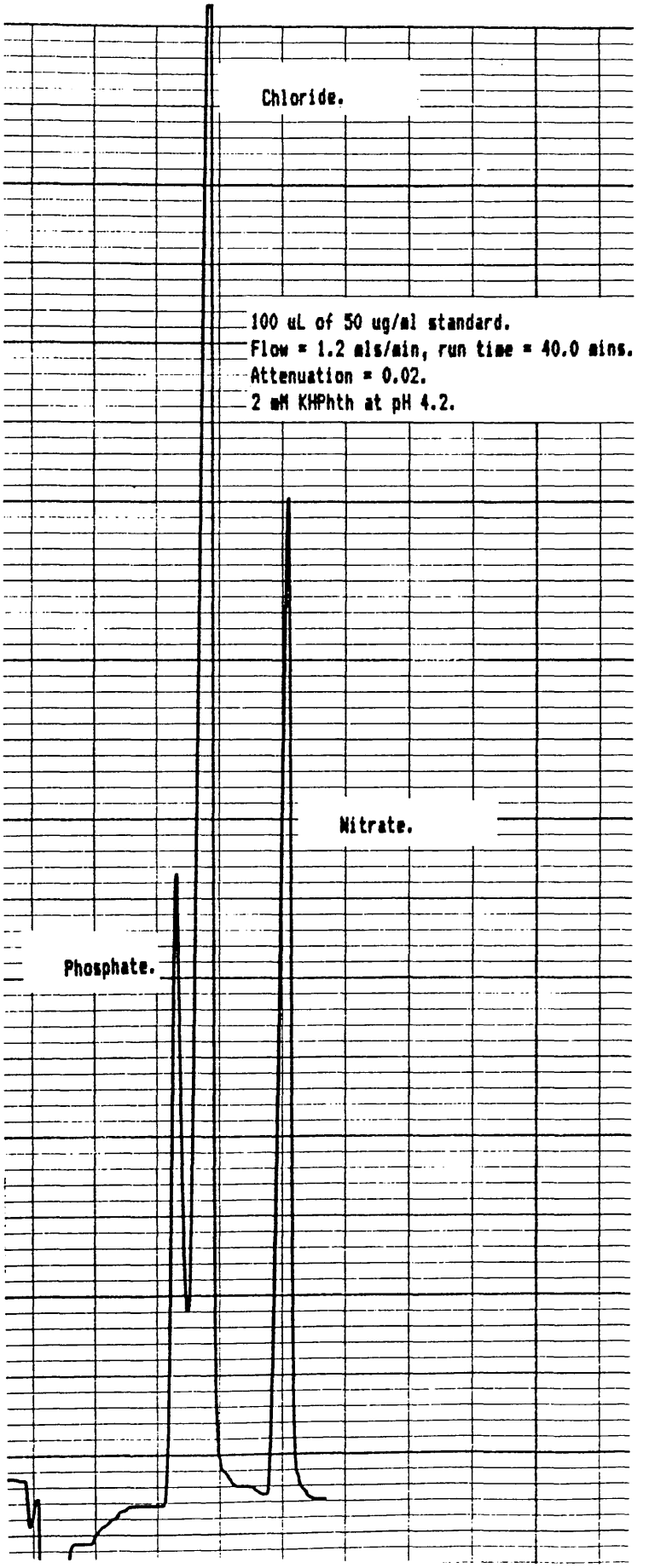
$$Cl = 0.28670 + 0.09922 * C3$$

$$NO3 = 0.58546 + 0.25147 * C5$$

$$SO4 = 0.28279 + 0.09269 * C7$$

C3 = Peak Height. C5 = Peak Height. C7 = Peak Height.

Figure 2.6. A Typical Anion HPLC Recorder Output Trace.


Chloride.
100 uL of 50 ug/ml standard.
Flow = 1.2 mls/min, run time = 40.0 mins.
Attenuation = 0.02.
2 mM KHPhth at pH 4.2.
Nitrate.
Phosphate.

Soil extracts were 0.45μm Millipore membrane filtered, but still contained sufficient unknown materials to provide variable baselines and column clogging. The main soil anions can be determined quite easily. Phosphate, however, is a problem, as, under the conditions used, it is mainly present as the $H_2PO_4^-$ species, and, hence, comes rapidly off the column, only slightly ahead of Cl^-, indeed, appearing as a shoulder on the chloride peak. Flow rates required to give sufficient phosphate peak resolution outweigh the benefits of this method; more work is required with this technique, probably using a different eluant and pH (Vydac, the manufacturers of the column, recommend a pH range of >2 but <7, so there is a restriction on how much above pH 4.2 we can go to improve the peak separation).

2.2.4. Additional Notes on Experimental Conditions

Throughout all the experiments in this study, only Analar regents and ashless filter papers (**Whatman no. 40**, 15.0 cm) were used. All bottles were washed in concentrated and 0.1M Nitric acid, and rinsed an appropriate number of times (usually 6) in distilled water until the washing water was at the same pH as the distilled water. All volumetric flasks, bulb pipettes, beakers and filter funnels were treated in a similar manner. When any apparatus was to be stored for any length of time, they were stored in, or contained, 0.1M Nitric acid. Plastic (**Azlon**) lab - ware was used as much as possible in equilibration experiments and solution preparations. Any standard solutions, in contact with volumetric glassware were transferred to pre-equilibrated plastic storage vessels as rapidly as possible, thereafter being refrigerated prior to use (<36 hours); no

standards over 48 hours old were used.

All pH measurements were carried out using a combination electrode (**Russell**) and a **Pye-Unicam** (model 262) pH meter, calibrated using pH 4.0 and pH 7.0 buffers.

In the centrifugal extraction of soil solution, the centrifuge used was an **MSE Mistral 2000** bench-top model with a swing-out rotor.

Chapter 3. Cadmium and Copper Sorption Isotherms.

3.1. The Sorption Process.

NB. in this, and subsequent chapters, it has been found necessary to resort to abbreviations for the soil names: the reduced forms are as follows;

Ark - Arkleston.

AHZ - Arkleston High Zinc.

Cap - Caprington

Dun - Dunlop

BA - Blackstoun Alluvial

Dreg - Dreghorn

FA - Fen Arable

FS - Fen Subsoil.

The data tables pertaining to this section may be found in appendix 2.

The removal of a metal from solution can be accomplished in several ways:

(a). Adsorption - a 2-dimensional process.

(b). Absorption - a 3-dimensional process.

(c). Precipitation - a 3-dimensional process.

The adsorption process may include ion-exchange reactions, whilst precipitation can include occlusion and co-precipitation. Sposito (1984), rightly pointed out that C versus X graphs, where C is the concentration in solution and X is the amount which has been removed from solution, and their various mathematical treatments, cannot be taken as definitive evidence for the action of any suggested mechanism. Thus, to avoid reading too much into data, all non-biotic processes which deplete the soil solution of a given cation or anion should be called 'sorption'. This may

be narrowed down to one of the above categories only by further experimentation. This approach is adhered to throughout this thesis.

The next stage in the investigation into the reactions of Cd and Cu in soil is the examination of the ways in which soils respond to changes in metal concentrations. As indicated in the previous chapter, the concentrations of Cd and Cu in the soils being used were very low, so any easily measurable amount added in an equilibration experiment will represent a significant increase in the quantity of the labile soil metal. Nonetheless, these may still be considered to be levels which moderate pollution of soil (ie. from aerial inputs, as opposed to deliberate introduction of metals via sludge use) would give rise to.

In the elucidation of the nature of the soil reaction, despite the need of spectroscopic evidence to confirm a mechanism, there are some chemical indicators which, in addition to the main determinand, may be followed in a sorption experiment which may help to define the reaction which is controlling the level of Cd and Cu in soil solution.

3.1.1. Observations on pH and Concentrations of Other Ions.

Several authors, as previously noted (section 1.3.4.3.), studied the influence of pH upon the retention of cations. More rare are reports of the influence which the sorption of metal ions has on the acidity of the solution. An ideal situation is visualized thus;

$$M^{2+}_{(aq)} + SOH_{2(s)} \iff SOM_{(s)} + 2H^{+}_{(aq)}$$

where the sorption of one divalent cation results in the displacement of two protons into solution. Either way, the sorption reaction is deemed to have a fixed stoichiometry. Given that a variety of species may possibly be sorbed (eg.

$M(OH)^+$) or that a highly specific site need not be protonated (it may be host to any number of cations, or even be of the form =N|-R or -|S|-R for example, in a protein or a Lewis base) this idealised approach could be thought of as being somewhat naive. However, in a background electrolyte which nullifies non-specific solute-surface interactions, to observe the release of protons in relation to metal uptake can give us an impression of the degree of importance of such sites, be they mineral or organic, in the specific retention of metals in soils.

Those authors who have described the pH changes taking place in soils on sorption of cations report that over two orders of magnitude of concentration, there is very little change in the suspension or supernatant pH coincident with heavy-metal removal from solution (Pulford 1986; pZn 3 - 5: Cavallaro and McBride 1978; pCu and pCd 6 - 4).

There is the possibility that the sorption of metal ions occurs by the displacement of other ions. A second option is that some form of precipitate is involved in determining the levels of the metals in the soil solution. Both situations are summarized thus;

$$1.\ AOH_{2(s)} + M^{2+}_{(aq)} <=> MOH_{2(s)} + A^{2+}_{(aq)}$$

$$2.\ MO_{(s)} + 2H^{+}_{(aq)} <=> M^{2+}_{(aq)} + H_2O_{(aq)}$$

A corollary of these reactions is the removal of anions with the cation on to a surface; this can be viewed from two angles - that of concommittant sorption, best seen schematically as

$$XOH_{2(s)} + Cu^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} <=> [XOH(Cu)SO_4]^{-}_{(s)} + H^{+}_{(aq)}$$

where the cupric and sulphate ions are discrete solution components; or of species sorption, the species in this instance being $(CuSO_4)^{\circ}_{(aq)}$.

Thus suggestions can be made as to the nature of the reaction which is proceeding by following the pH and metal ion concentration changes at equilibrium, along with the status of the solution with respect to anions: the ideal chemical study of such a system should comprise all the above named features.

A concept which has been widely applied the work of Lindsay (1979), is to plot the activity of the cation being studied against the equilibrium pH of the system. In its application, this idea meets with two problems:

(a). The measurement of free ion activity.

Stability constants, as quoted in such standard reference texts as Lindsay (1979) and Baes and Mesmer (1976) are given in terms of activities (although the latter does include some concentration based quotients) which have to be amended to concentration terms, or the data have to be translated into activities, before these constants can be used in a predictive sense.

(b). The measurement of pH.

The considerations of soil pH have been outlined in the introductory chapter (section 1.3.4.3.). In a given experiment three different measures of the soil pH could be made: the slurry, the supernatant above the slurry and the separated supernatant. The problem involved is clearly demonstrated by considering the following: a soil mineral, Cupric Ferrite is posited as controlling the level of Cu^{2+} in soil solutions;

$$Fe_2CuO_{4(s)} + 8H^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Fe^{3+}(aq) + 4H_2O$$

$$K^\circ \equiv \frac{(Cu^{2+})(Fe^{3+})^2}{(H^+)^8} = 10^{10.13}$$

Thus, $[\log (Cu^{2+}) + 2\log (Fe^{3+})] = 10.13 - 8pH.$

In terms of a solubility diagram, plotting the term in square brackets (y-axis) against pH (x-axis) a graph of gradient - 8 and y-intercept of 10.13 is obtained. If experimental data are plotted, the activities of Cu and Fe will be pH dependent, so which pH will we use? Similarily, which pH should be plotted on the x-axis? For this study it has been reasoned that since all the determinations which were performed (for metals, by AAS) used supernatants, therefore the separated supernatant pH is applicable.

Two sets of sorption isotherms were executed, one at a relatively high level of metal addition (up to mM) and one at a relatively low (μM). Once it became established that the behaviour of the soil-metal system could be well described, a range of concentrations for further study were selected.

Additionally, the effect of ashing the soil, to eliminate organic matter contributions to uptake, and the influence of the initial pH of the solution used in the equilibrium were examined.

3.2. Materials and Methods.

3.2.1. Sorption Experiments.

The initial set of sorption isotherms comprised 12 different concentrations of Cu and Cd (nominally 6, 8, 10, 20, 40, 60, 80, 100, 200, 400, 600 and 800 μM for Cu and 7, 9, 18, 36, 53, 72, 89, 178, 356, 534 and 712 μM for Cd) in a background electrolyte of 0.1 M $NaNO_3$. This background salt was chosen for two reasons;

(a) elimination of non-specific reactions by Cu and Cd by mass action swamping of generally low-affinity sites.

(b) to maintain a high ionic strength so that the only changes in speciation would be due to changes in pH or M^{2+}.

2g of air-dry soil were shaken for 24h (end-over shaker) with 50ml of each solution in 150ml plastic bottles. Following this, the pH was measured in the slurry (stirred) using the pH apparatus detailed in section 2.2.4. The suspensions were then filtered using Whatman no. 40 (fluted 15.0cm) on polythene filter funnels and the filtrates collected in 60ml polythene bottles. These solutions were then analysed for Cu or Cd, dilutions being performed where necessary, with the ionic strength of the diluted solutions being maintained at 0.1.

With the second set of isotherms, the concentration range was reduced to: Cd and Cu 0, 1, 2, 3, 7, 15, 20, 30, 40, 60, 75 and 90 μM, again in 0.1M $NaNO_3$. With this set, pH was also determined in the supernatant, and ISE measurements (equipment as in section 2.2.2) were conducted both in the suspensions and supernatants. On analysis by AAS, Fe and Mn were measured in the six "acidic" soils, whilst Ca and Fe were quantified in the calcareous ones.

The data derived from these experiments were then subjected to various mathematical treatments (Langmuir, van Bemmelen-Freundlich) in an attempt to give a broad description of the sorption process.

3.2.2. Influence of Organic Components.

From the above two experiments, three soils were chosen for further studies: Arkleston, Arkleston High Zinc and Fen Arable due to their wide range in composition and behaviour.

In an investigation to clarify the importance of the sorbed organic and soluble organic fractions to metal relations in the soil, an experiment was undertaken to monitor the sorption of traces of Cu and Cd on to soil which

had the organic component removed. The method chosen for organic matter removal was the same as used in the loss on ignition experiment ie. placing soil in an oven at 550°C for 5h: this method is favoured above the use of peroxide for organic matter destruction, as this would require much washing to remove the oxidation detritus, such as oxalates, which would easily bring about metal precipitation

2g of the ashed material were shaken with 50ml of 5, 10, 15, 20, 25 and 30 μM Cu or Cd in 0.1M $NaNO_3$ for 24h. Equilibrium pH was measured in the filtrate and Cu or Cd determined by AAS. These figures were compared with the whole soil.

Each g of air-dry soil is equal to (via LOI figures):

(a). 1.085 g of Arkleston

(b). 1.110 g of Arkleston High Zinc

(c). 1.125 g of Fen Arable

3.2.3. Influence of pH.

The effect of setting the solution pH before equilibrium with soil was examined. A fixed concentration of Cu or Cd was chosen (15μM) and the pH range of 4 to 8 was selected for study (this being roughly the range encountered in UK soils). Again, 2g of air-dry soil was suspended in 50ml of solution and shaken for 24h. The pH was measured in the filtrate and then Cu or Cd was measured by AAS.

3.3. Results and Discussion.

3.3.1. Sorption Isotherms.

3.3.1.1. Batch Isotherms by AAS.

For both copper and cadmium, a general trend can be observed if the full isotherms are examined: (Figure 3.1. a,b and 3.2. a,b) Arkleston (Ark), Dreghorn (Dreg), Arkleston High Zinc (AHZ), Dunlop (Dun) and Caprington (Cap) all give rise to L-type isotherms, whilst Blackstoun (BA) and the two Fen (FA and FS) soils are of the H type. In order of affinity (from the relative shapes of the graphs) this produces the sequence :

FA > FS > BA > Dun > Cap > Ark > Dreg > AHZ for Cu and

FA > FS > BA > Cap > Dun > Ark > Dreg = AHZ for Cd

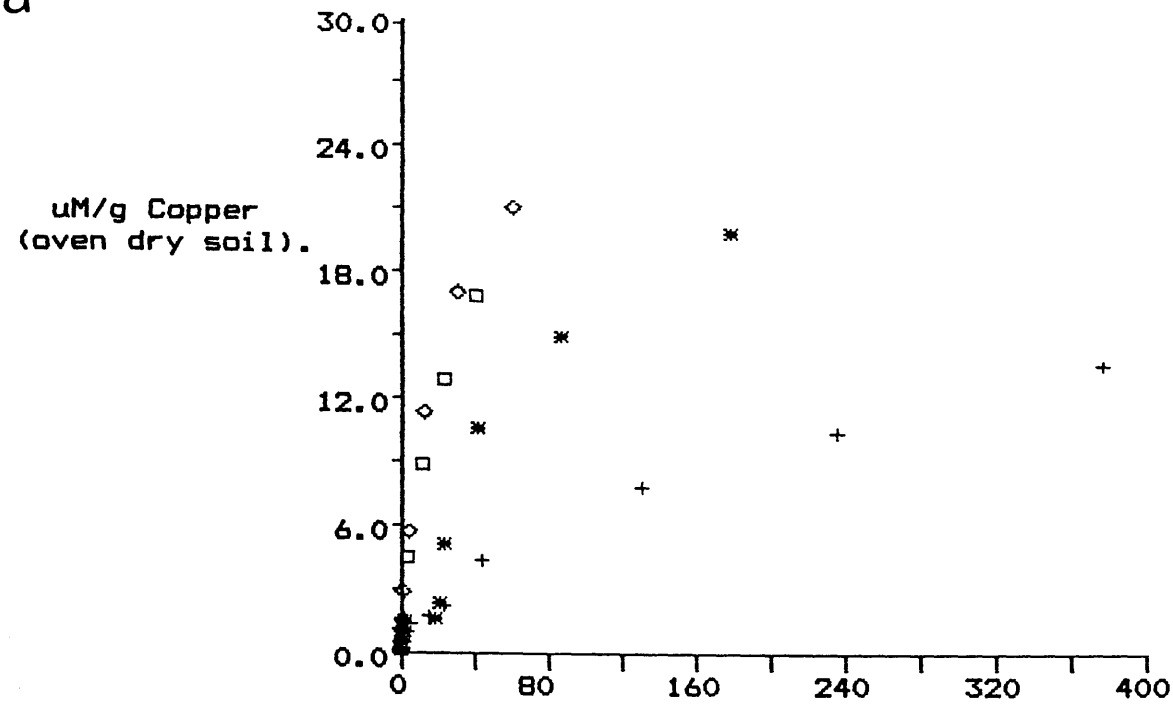
The pattern of affinity is largely the same for both metals, however, on a mole for mole comparison, it would appear that much more Cu was taken up by soils than Cd. As both sets of data have a conglomeration of points in the lower corner of the graph, it is of importance that this low level area is examined to see if the overall sorption pattern is maintained. On a 67x expansion for Cd and a 300x expansion for Cu (Figures 3.3. a, b and 3.4. a,b), the fine detail of the sorption can really be seen.

Figures 3.1. and 3.2. Copper and Cadmium Sorption Isotherms.

Figure 3.1. Cu Sorption (a). Ark, AHZ, Cap and Dreg.
(b). BA, Dreg, FA and FS.

Figure 3.2. Cd Sorption (a). Ark, AHZ, Cap and Dreg.
(b). BA, Dreg, FA and FS.

a

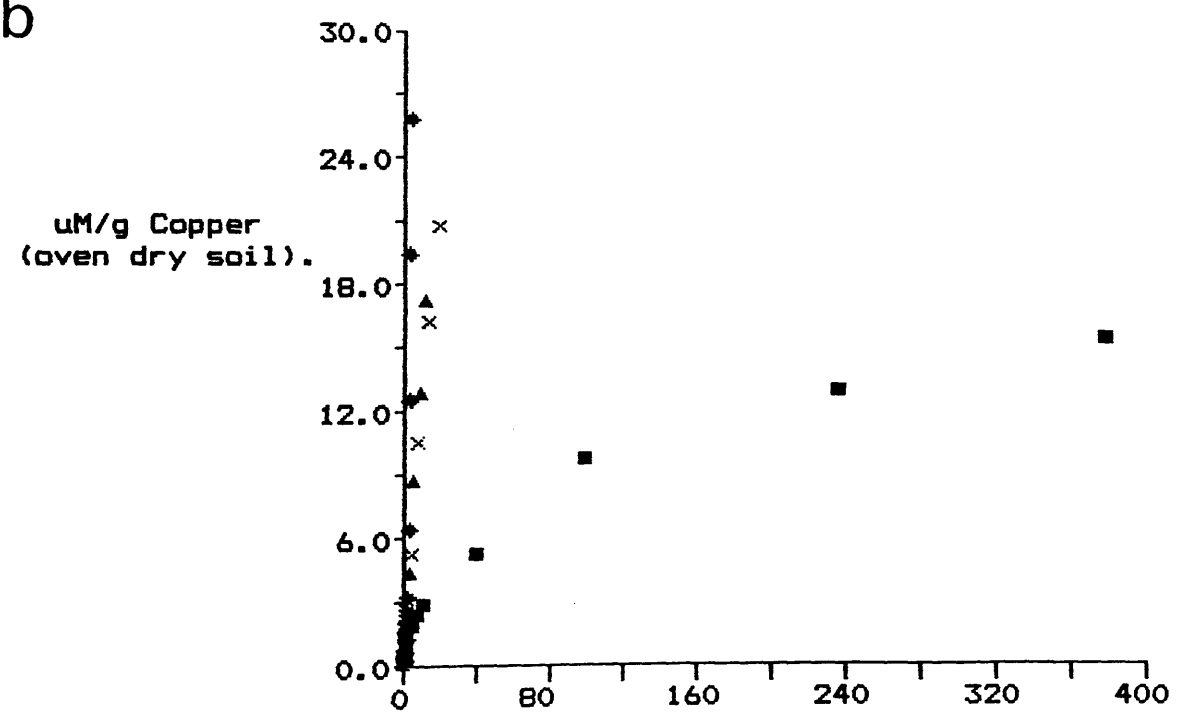


Copper uptake in 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b

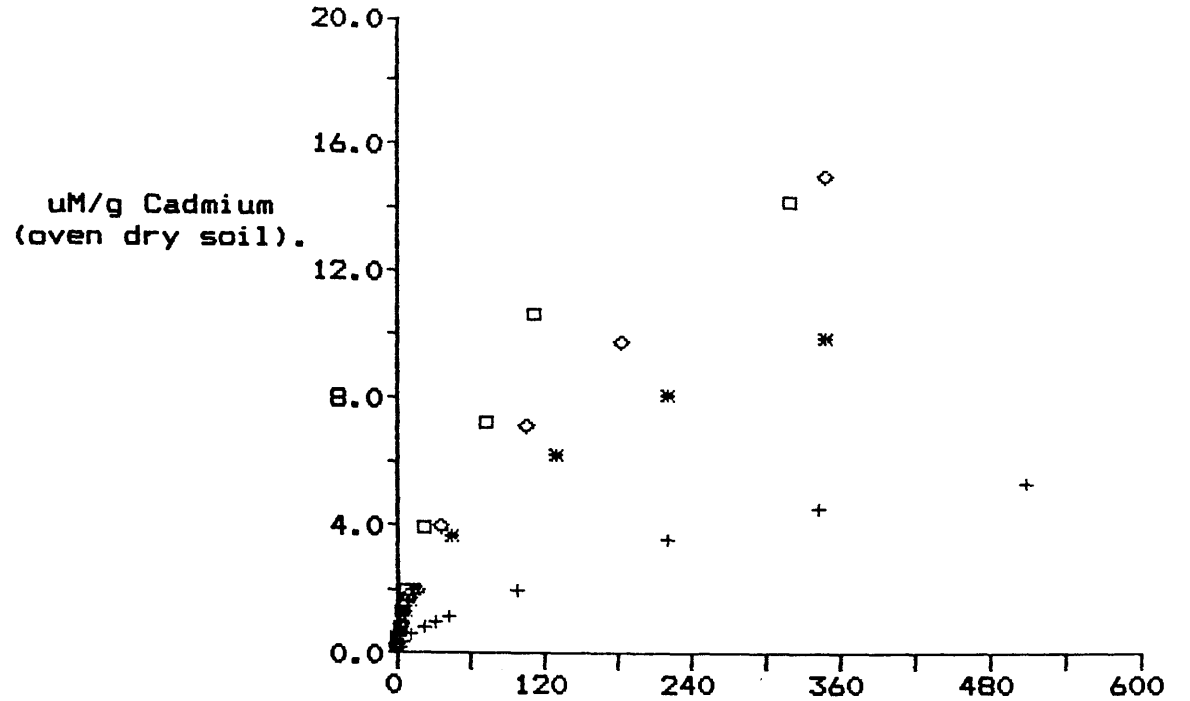


Copper uptake in 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

a

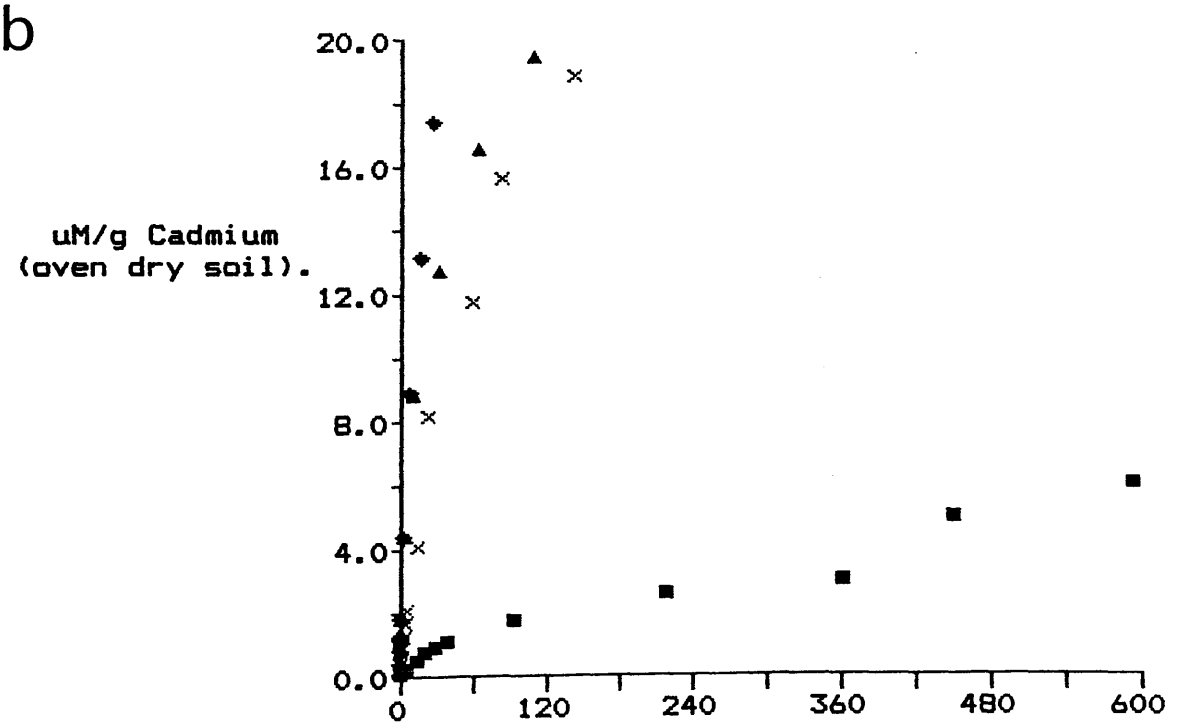


Cadmium uptake in 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



Cadmium uptake in 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Figures 3.3. and 3.4. Expanded Lower end of Copper and Cadmium Sorption Isotherms.

Figure 3.3. Expanded Lower end of Cu graph

(a). Ark, AHZ, Cap and Dun.

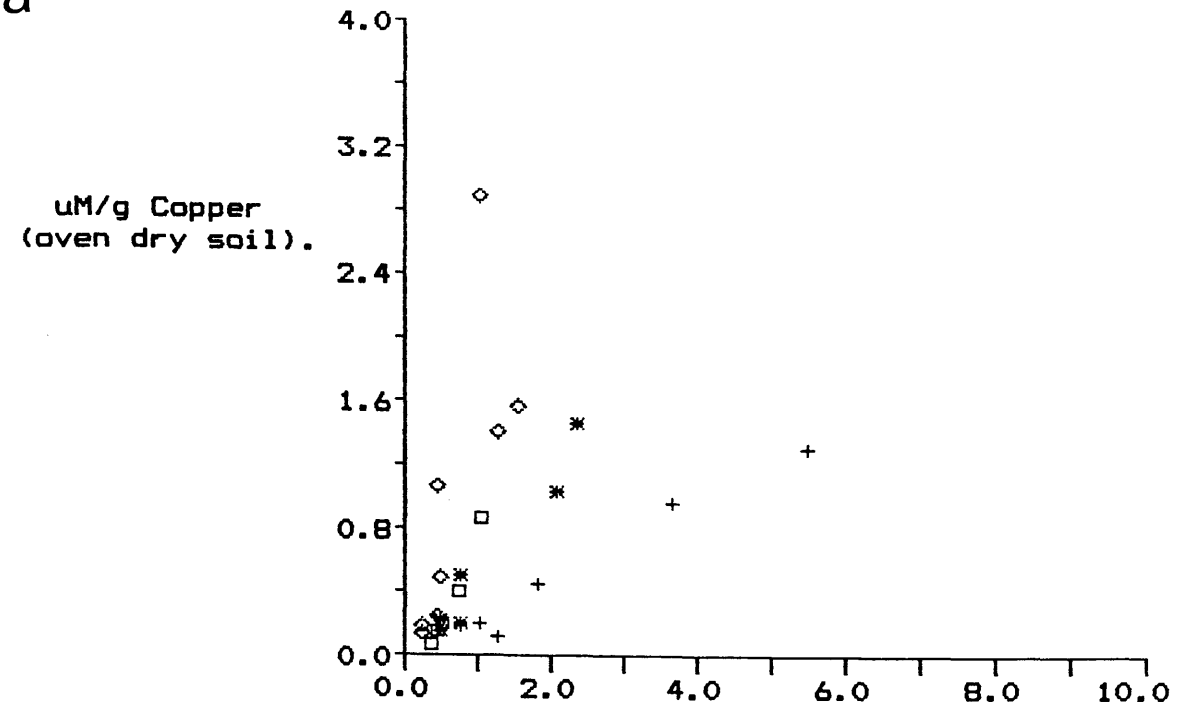
(b). BA, Dreg, FA and FS.

Figure 3.4. Expanded Lower end of Cd graph

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

a

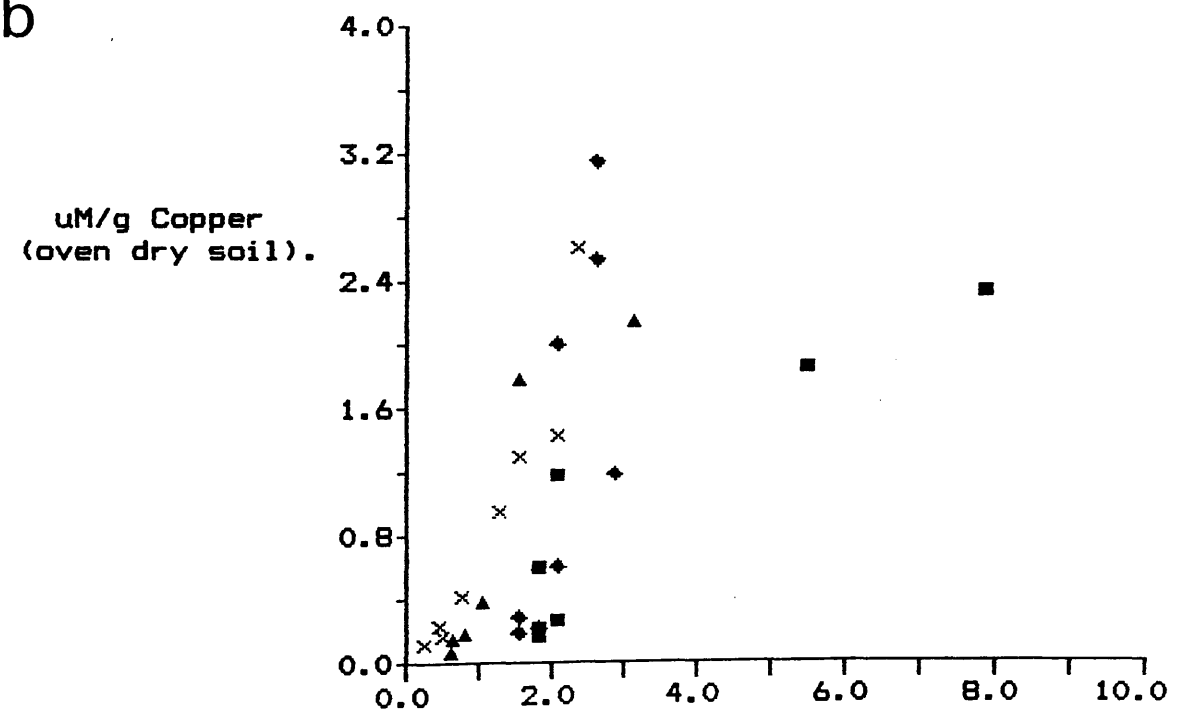


Copper uptake in 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b

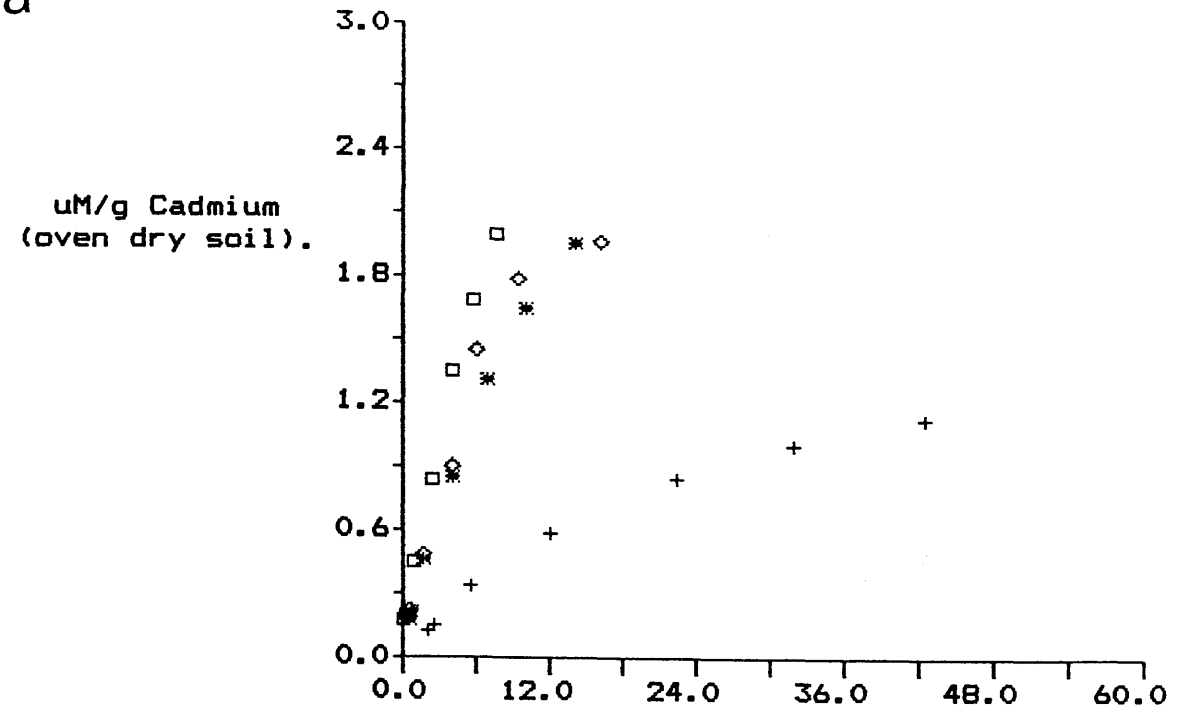


Copper uptake in 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

a

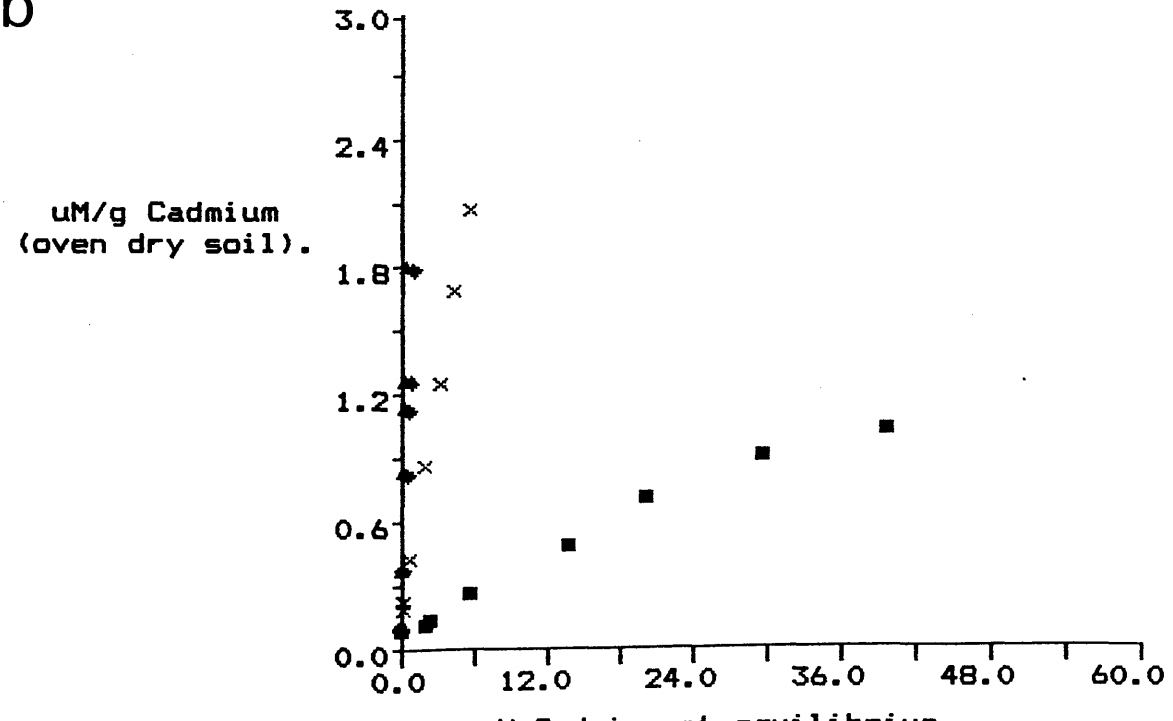


Cadmium uptake in 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



Cadmium uptake in 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

There is a fair degree of scatter with the Cu points, but overall it can be seen that all of the graphs appear to be intersecting with the x-axis at values greater than zero, implying a native soil contribution to the total copper present. The L- and H-character of the isotherms has been replaced by, in most cases, a C-type, implying that the levels of Cu present were all well below the soils saturation capacity. The Fen Subsoil and Blackstoun soils both demonstrate S character which is indicative of a solution resevoir (ie. soluble organic matter) maintaining solution levels at greater concentrations than would be expected, until at a higher concentration this sink is filled and the added Cu is taken up on to surfaces (> 0.5 μM for Blackstoun, > 0.8 μM for Fen Subsoil).

The order of uptake at these concentrations shows some changes, which could be due to differences in the amount of soluble organic matter which is present, the order being: Dun > Cap > ArK > FA > BA> FS > Dreg > AHZ.

At the lower end of the cadmium isotherms, the affinity order is largely maintained;

FS > FA >BA > Cap >ArK > Dreg = AHZ.

The Fen soils all demonstrated a very high affinity for Cd, the low level end of the isotherm being an H-form, whilst the others were L-forms. Comparing this with the copper situation it can be inferred that soluble organic matter had little influence on the levels of Cd in solution, whilst confirming the observations of Papadopoulos and Rowell (1988) and Santillan-Medrano and Jurinak (1975) that the carbonate content of soils is instrumental in a highly specific removal of Cd from equilibrating solutions. Comparing the gradients of copper and cadmium isotherms showed that those for copper were greater at the low levels

than those for cadmium, implying a greater soil affinity for copper. This trend is reversed for the two Fen soils, which strengthens further the case for the role of calcium Carbonate for determining solution Cd levels in these soils.

As no single, simple equation relating C and X could be used to summarise the data, an attempt was made to describe the system by a Langmuir equation (Figure 3.5. a-d: Cd, and 3.6. a,b: Cu). For copper, quite clearly, this approach failed. Unless only equilibrium concentrations greater than about 20 μM Cu are considered, the isotherm is in no way a linear one. All of the isotherms have an initial downward slope, a turning point, and then a more normal linear section which could be used for the calculation of Langmuir constants. This type of plot for the Langmuir isotherm has been proposed as having its origins in a precipitation reaction (Veith and Sposito, 1977): two points militate against this;

(a). Minimal change in pH

(b). The concentrations of the other main co-precipitants Mn, Fe and Ca did not change in any regular (stoichiometric) manner (see Table 3.1. for summary of results).

This does not rule out the possibility of precipitation altogether, or precipitation-like reactions: consider the soil bound organic matter, the high equilibrium constants for Cu binding to these species may be so great as to constitute precipitation.

Figures 3.5. and 3.6. Langmuir Plots of Cd and Cu Sorption Data.

Figure 3.5. Langmuir Plot of Cd Data.

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

(c). Expanded view of (a).

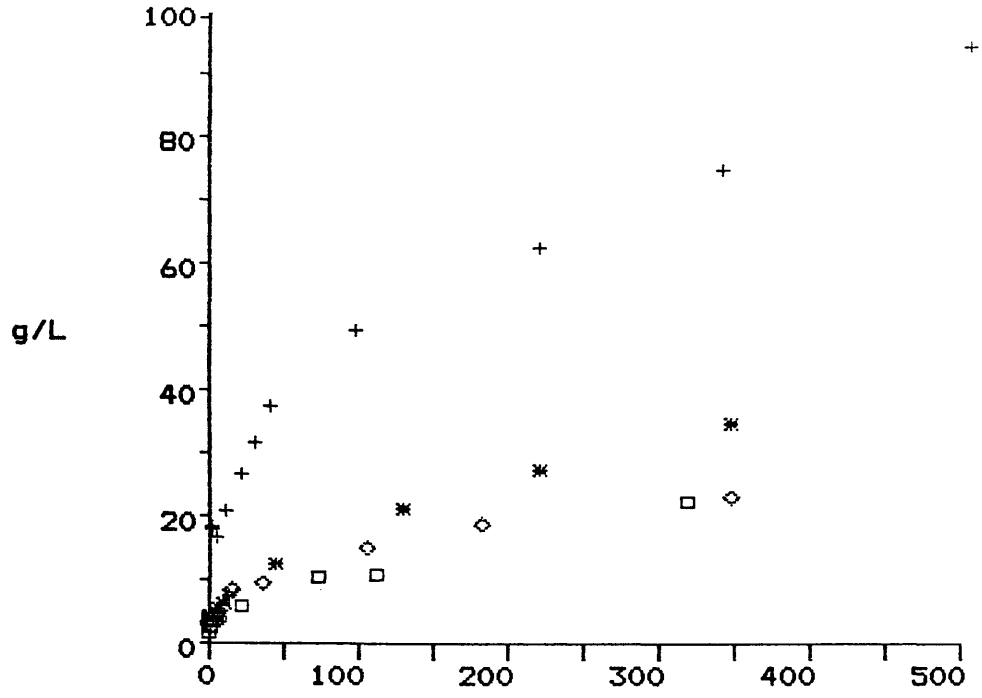
(d). Expanded view of (b).

Figure 3.6. Langmuir Plot of Cu Data.

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

a



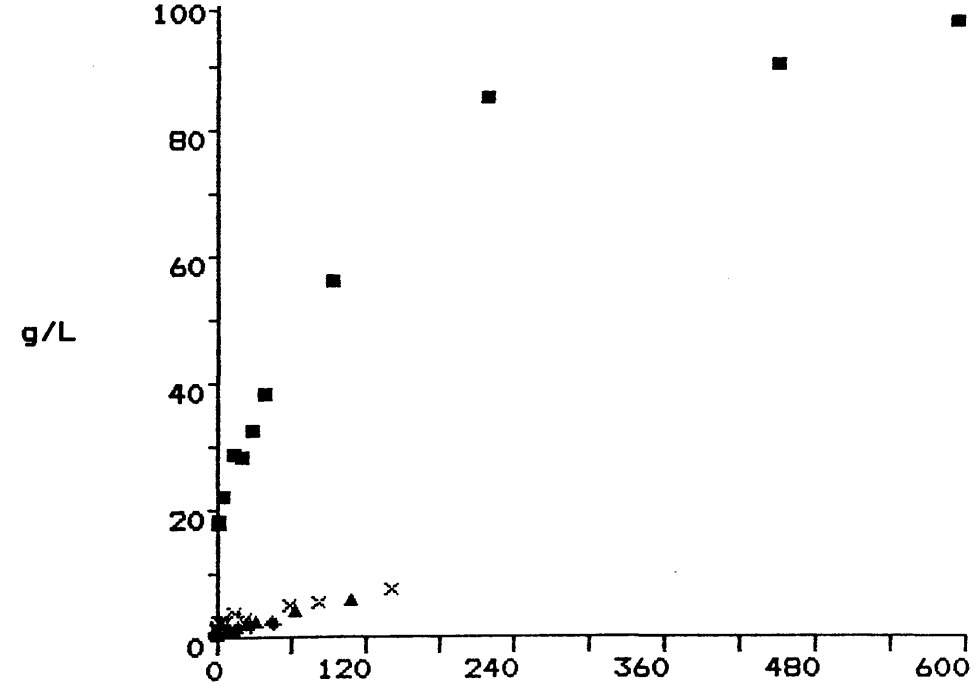
uM Cadmium at equilibrium.

Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



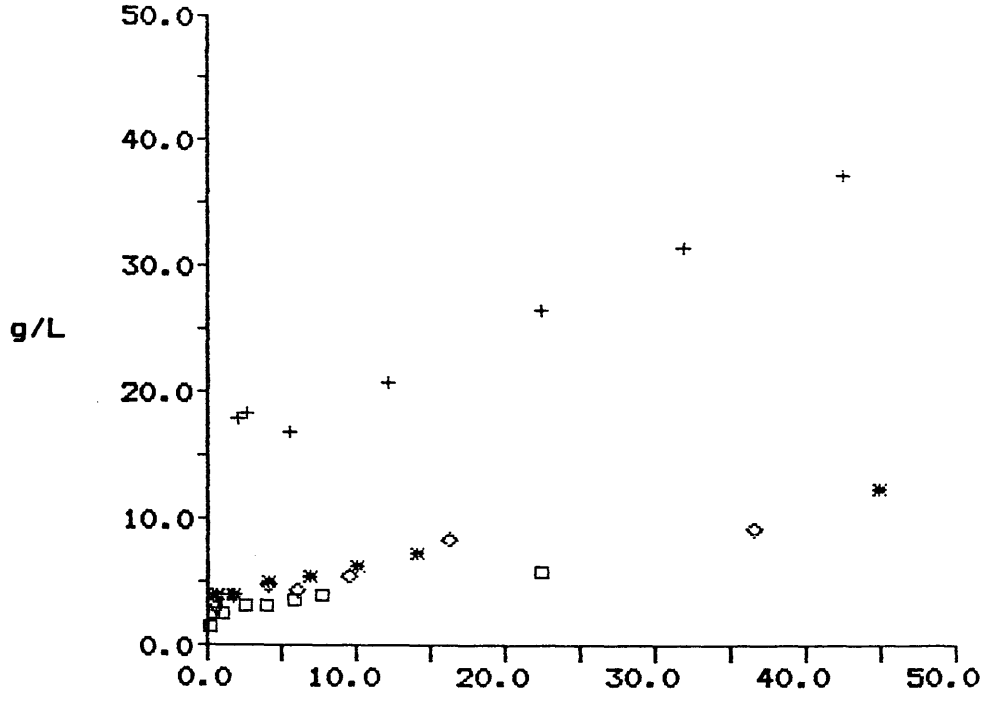
uM Cadmium at equilibrium.

Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

c

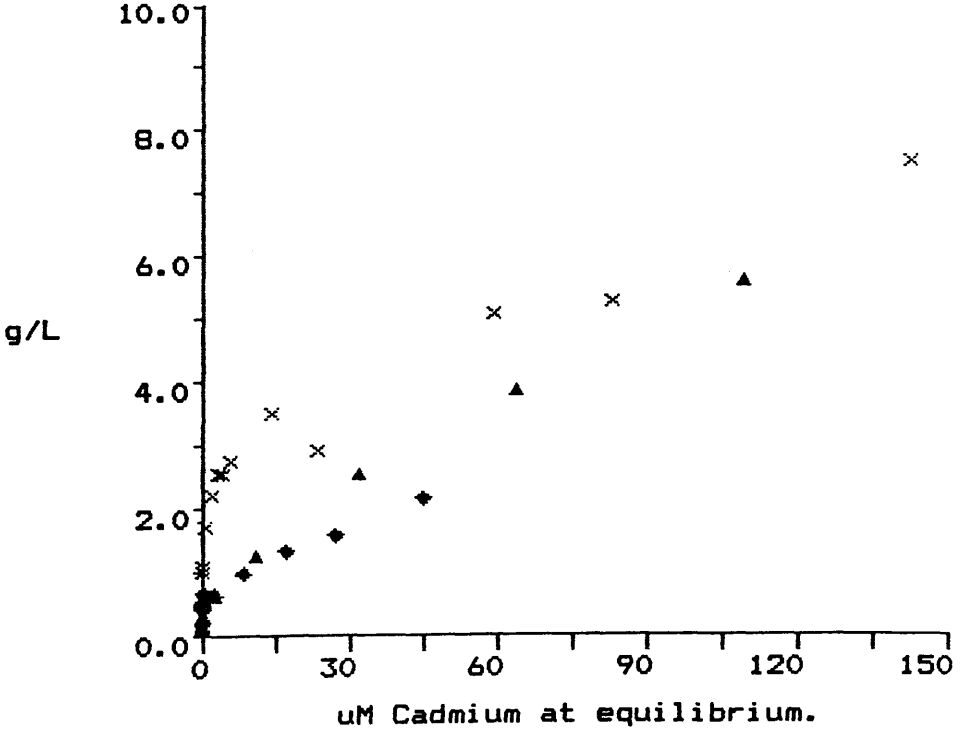


Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

d

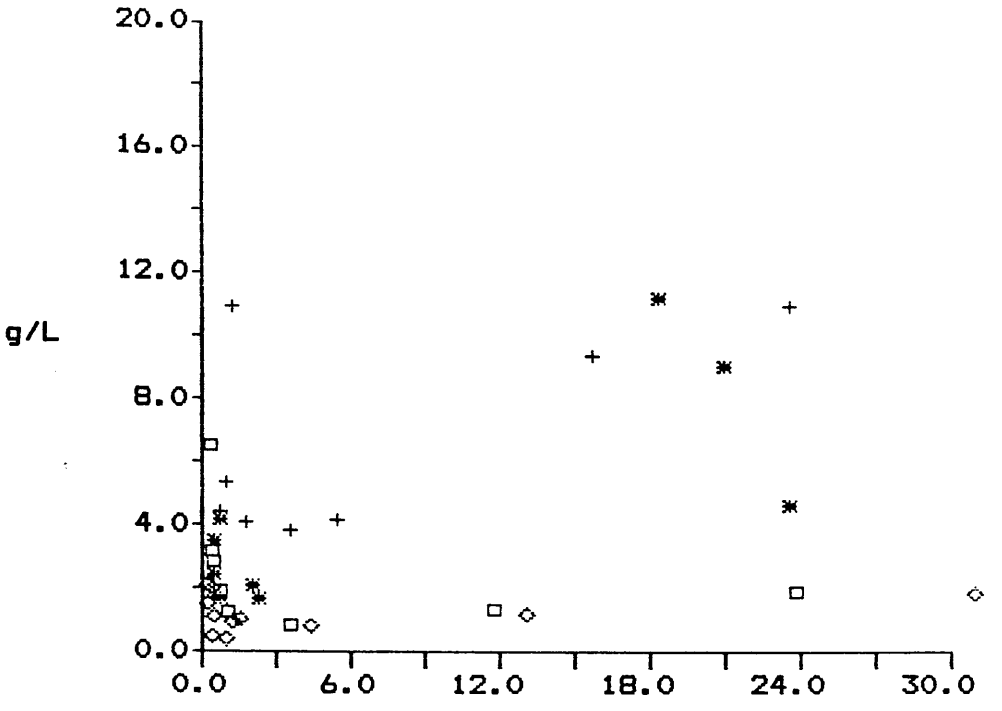


Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

a

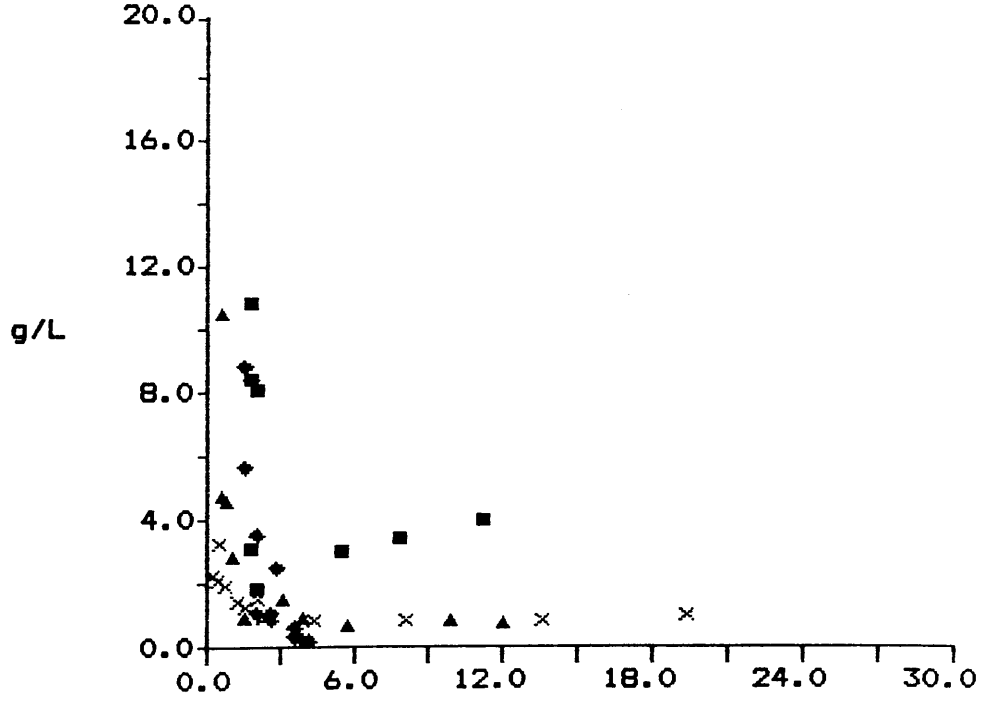


Copper uptake in 0.1M NaNO3:Langmuir isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



Copper uptake in 0.1M NaNO3:Langmuir isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Table 3.1. Isotherms: 1, lowest part of graph.

COPPER

Soil	Equation	No. Points	r^2
Ark	X = 0.64C - 0.16	6	0.942
AHZ	X = 0.26C - 0.08	6	0.972
Cap	X = 1.36C - 0.55	6	0.998
Dun	X = 1.28C - 0.04	9	0.883
BA	X = 1.14C - 0.24	12	0.990
Dreg	X = 0.28C - 0.005	8	0.886
FA	X = 0.76C - 1.02	5	0.949
FS	X = 1.14C - 0.65	7	0.912

CADMIUM

Soil	Equation	No. Points	r^2
Ark	X = 0.14C - 0.19	7	0.971
AHZ	X = 0.04C - 009	5	0.969
Cap	X = 0.25C - 0.16	7	0.985
Dun	X = 0.18C - 0.12	6	0.977
Ba	X = 0.32C - 0.17	9	0.989
Dreg	X = 0.03C - 0.11	7	0.976
FA	X = 1.59C - 0.05	8	0.997
FS	X = 3.52C - 0.07	7	0.987

The cadmium data can be described quite well by means of a two-constant Langmuir approach. It is difficult to quantify these curves, other than by describing the data by the two best fitting straight lines and deriving the two-constant equation accordingly - table 3.2.

Table 3.2. Isotherms: 1, Two-Constant Langmuir Examples for Cadmium.

Arkleston High Zinc	$K_1 = 0.031$	$K_2 = 0.003$
	$X_1m = 2.077$	$X_2m = 8.444$
Caprington	$K_1 = 0.153$	$K_2 = 0.013$
	$X_1m = 3.378$	$X_2m = 17.727$
Dunlop	$K_1 = 0.102$	$K_2 = 0.004$
	$X_1m = 3.295$	$X_2m = 23.773$
Dreghorn	$K_1 = 0.020$	$K_2 = 0.000$
	$X_1m = 2.489$	$X_2m = 30.797$
Fen Arable	$K_1 = 2.573$	$K_2 = 0.080$
	$X_1m = 2.801$	$X_2m = 20.851$

K_n and X_nm being curve fitting parameters which have been described as the Langmuir bonding constant and the Langmuir maximum adsorption respectively.

As Sposito (1982) has remarked, though, the fitting of a two-constant form of the Langmuir equation is not indicative of two surfaces being involved in the reaction: this view has also been put forward by Posner and Bowden (1980). If the data are treated according to the van Bemmelen-Freundlich isotherm (Figure 3.7. a, b) a high measure of success is achieved for Cd: over three orders of magnitude equilibrium concentration, the isotherms were quite linear (Table 3.3., gradients, intercepts and r^2 values). All the ß values (gradients) were less than 1.0 as required in Sposito's derivation of the equation.

Copper, meanwhile, continues to defy simple efforts to

linearize the data, producing curves (see Figure 3.8. a,b). The lower portion of the isotherm is very steep, and the gradients are greater than 1.0 (Table 3.3 shows gradients of both portions).

Table 3.3. Isotherms: 1, Freundlich.

COPPER

Soil	Low Equation	r^2	High Equation	r^2
Ark	logX = 1.33.logC - 0.37	0.880	logX = 0.664.logC - 0.25	0.879
AHZ	logX = 1.20.logC - 0.76	0.861	logX = 0.590.logC - 0.38	0.980
Cap	logX = 2.46.logC - 0.11	0.970	logX = 0.900.logC - 0.11	0.945
Dun	logX = 1.42.logC - 0.06	0.712	logX = 0.650.logC + 0.24	0.934
BA	logX = 1.43.logC - 0.21	0.975	logX = 1.000.logC + 0.07	0.993
Dreg	logX = 5.11.logC - 1.90	0.212	logX = 0.510.logC - 0.09	0.996
FA	logX = 4.18.logC - 1.47	0.715	logX = 3.700.logC - 1.02	0.890
FS	logX = 3.28.logC - 0.44	0.995	logX = 1.200.logC - 0.08	0.934

CADMIUM

Soil	Low Equation	r^2
Ark	logX = 0.65.logC - 0.54	0.981
AHZ	logX = 0.72.logC - 1.09	0.979
Cap	logX = 0.69.logC - 0.35	0.965
Dun	logX = 0.71.logC - 0.50	0.970
Ba	logX = 0.73.logC - 0.23	0.995
Dreg	logX = 0.66.logC - 1.09	0.989
FA	logX = 0.80.logC + 0.15	0.989
FS	logX = 0.59.logC + 0.26	0.976

Figures 3.7. and 3.8. Freundlich Plots of Cd and Cu Sorption Data.

Figure 3.7. Freundlich Plot of Cd Data.

(a). Ark, AHZ, Cap and Dun.

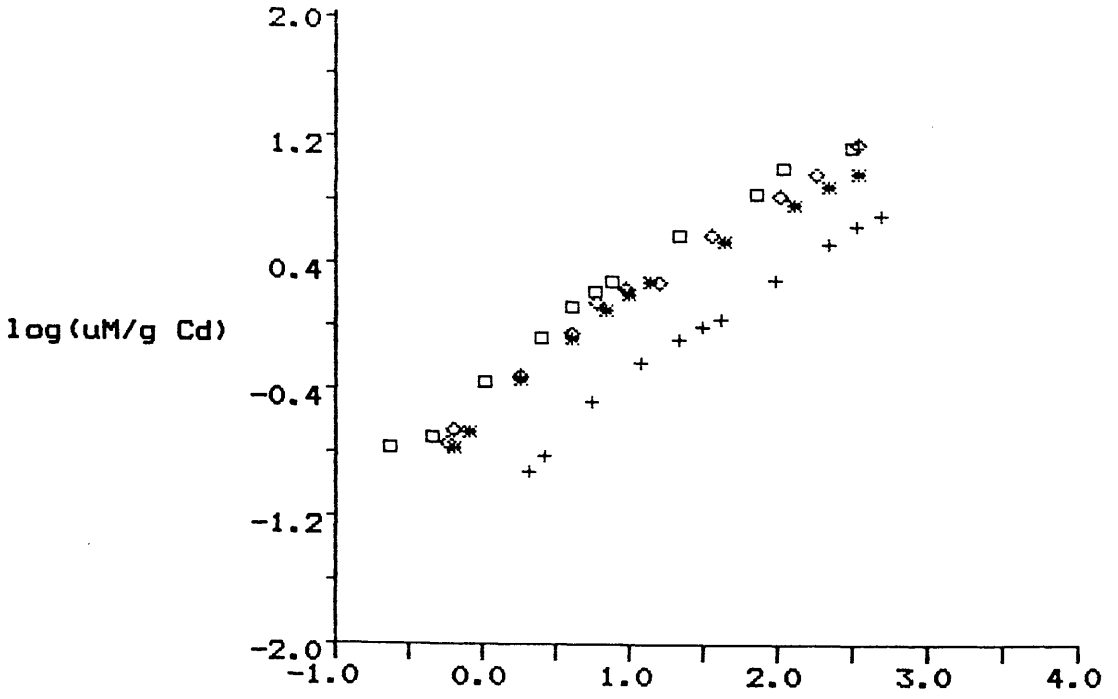
(b). BA, Dreg, FA and FS.

Figure 3.8. Freundlich Plot of Cu Data.

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

a

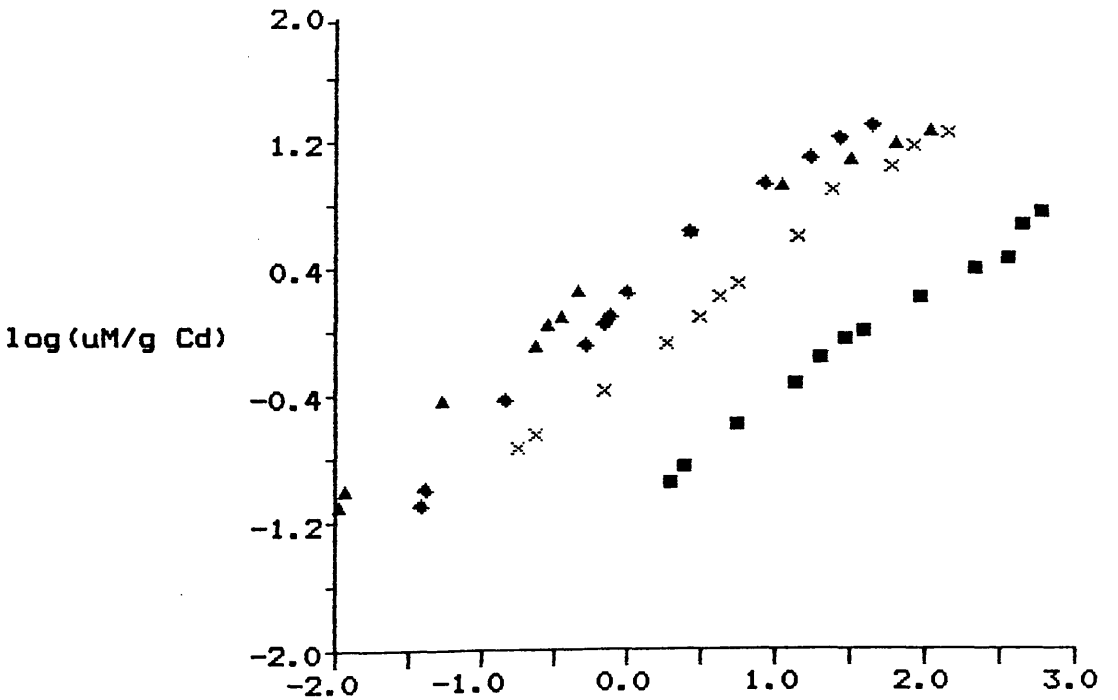


Cadmium uptake in 0.1M NaNO3:Freundlich isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b

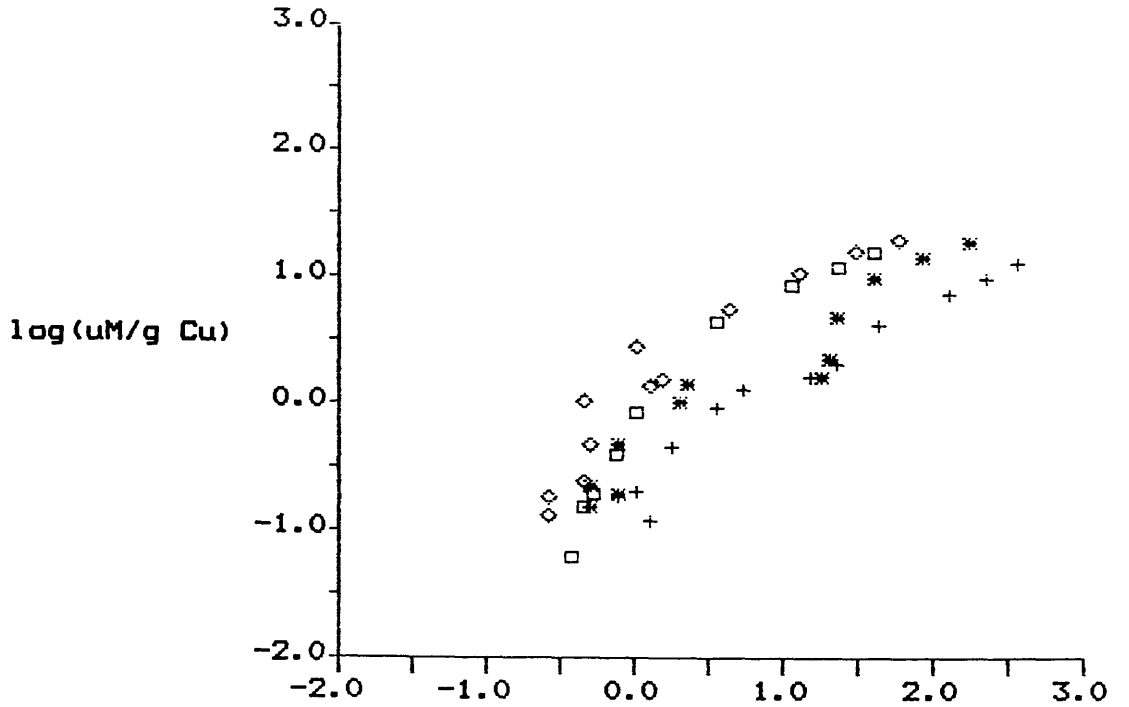


Cadmium uptake in 0.1M NaNO3:Freundlich isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

a

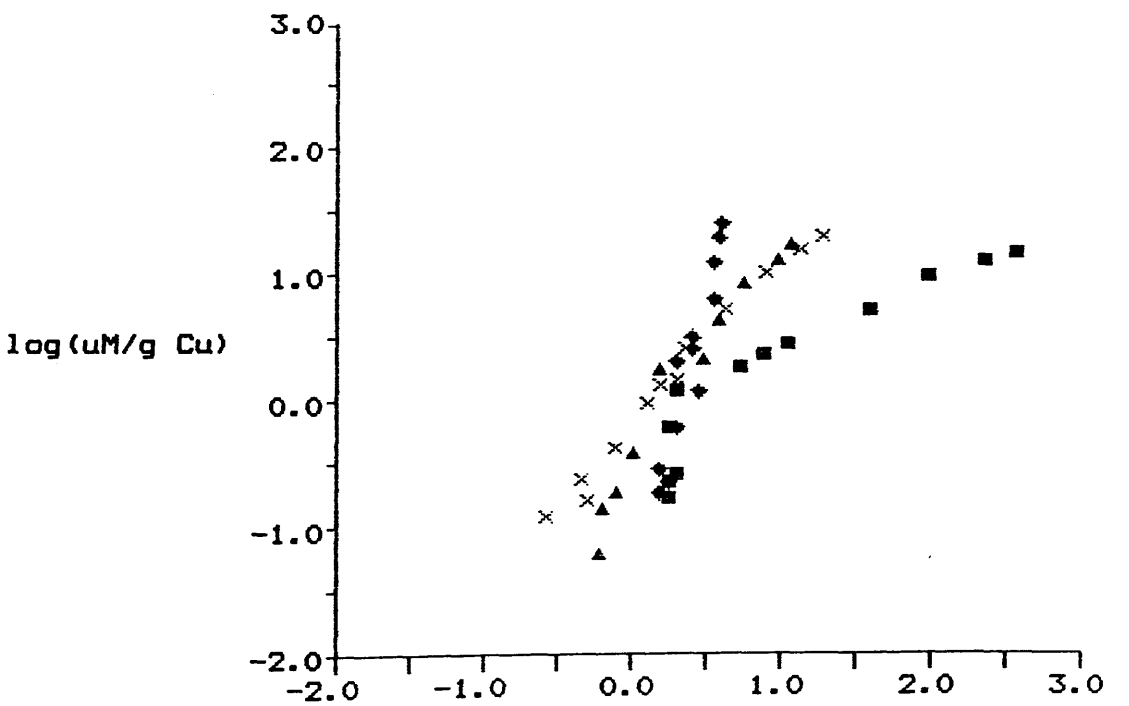


Copper uptake in 0.1M NaNO3:Freundlich isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



Copper uptake in 0.1M NaNO3:Freundlich isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

The curvature could be due to the influence of the soluble organic matter which would tend to decrease the gradient of the graph at the lower end; but, as this is absent from the C v X isotherms of five out of eight of the soils, this appears to be only partly responsible. Furthermore, the van Bemmelen-Freundlich "break" is not related to the change in gradient point of the C v X S-type isotherms. Jarvis (1981) also found quite a marked change in gradient in his Cu Freundlich isotherms in calcareous soils, which he attempted to account for in terms of CO_3^{2-} and HO^- speciation of the Cu. As shown in section 1.2.3., the speciation of Cu is quite labile. However, with these isotherms, 90% plus of the Cu in solution is being sorbed, and, at the pH's involved, the presence of other species over and above $(Cu^{2+})_{free}$ is of the order of 10%, thus it seems unlikely, unless changes in the very rapidly equilibrating system are being monitored, that the inorganic speciation is influencing this isotherm to any great degree. The curvature probably represents a combination of organic and inorganic speciation functions.

3.3.1.2. Batch Isotherms by AAS and ISE.

The low end of the sorption isotherm was examined in these experiments: initially the AAS derived measurements will be discussed. Patterns of uptake were observed which tended to imply that soluble organic matter was exerting an influence upon solution levels of copper: with these isotherms, S-type behaviour for both Fen soils, Blackstoun and Caprington can be seen. This coincides with the notions of;

(a). High levels of organic matter

(b). High soil pH giving rise to high levels of soluble

organic matter.

Dreghorn and Arkleston high Zinc display L-type isotherms, whilst Dunlop and Arkleston have C-shape graphs: again, all the isotherms have x-axis intercepts at values > 0. For this series of curves, the relative order of affinity is:

Dun> Dreg > Ark > AHZ > FA > BA > Cap = FS

(see fig. 3.9. a-d).

This order is different from the low order expansion and the overall isotherms at high levels (described in section 3.3.1.1.) - FA, FS, BA and Cap now appearing at the right of the series. A pattern seems to be emerging in which the high pH effect of the Fen soils, causing high affinity for Cu, is being overcome by the release of organic matter into solution, and the more mineral soils are assuming a dominant position in the affinity series, whilst for soil pH's<5.5, the relatively high organic matter contents of BA and Cap play a role in the solution chemistry.

As previously noted, the low end of the cadmium isotherms in the acidic soils portray L-type lines, whilst the high pH Fen soils display H-character isotherms. At very low levels of Cd soluble organic matter might be expected to play a role in the solution relationships of Cd, but the only evidence of this is with the Blackstoun soil, although this may be a function of the scatter of the experimental points.

The Cd affinity order is;

FS > FA > Cap > BA > Dun = Ark > Dreg = AHZ (fig. 3.10. a-d).

This is quite similar to that seen in section 3.3.1.1.

The gradients and intercepts of the C v X isotherms are summarized in table 3.4.

Figures 3.9 and 3.10. Copper and Cadmium Sorption Isotherms.

Figure 3.9. Cu Sorption (a). Ark, AHZ, Cap and Dreg.

(b). BA, Dreg, FA and FS.

Figure 3.9. Expanded Lower end of Cu graph

(c). Ark, AHZ, Cap and Dun.

(d). BA, Dreg, FA and FS.

Figure 3.10. Cd Sorption (a). Ark, AHZ, Cap and Dreg.

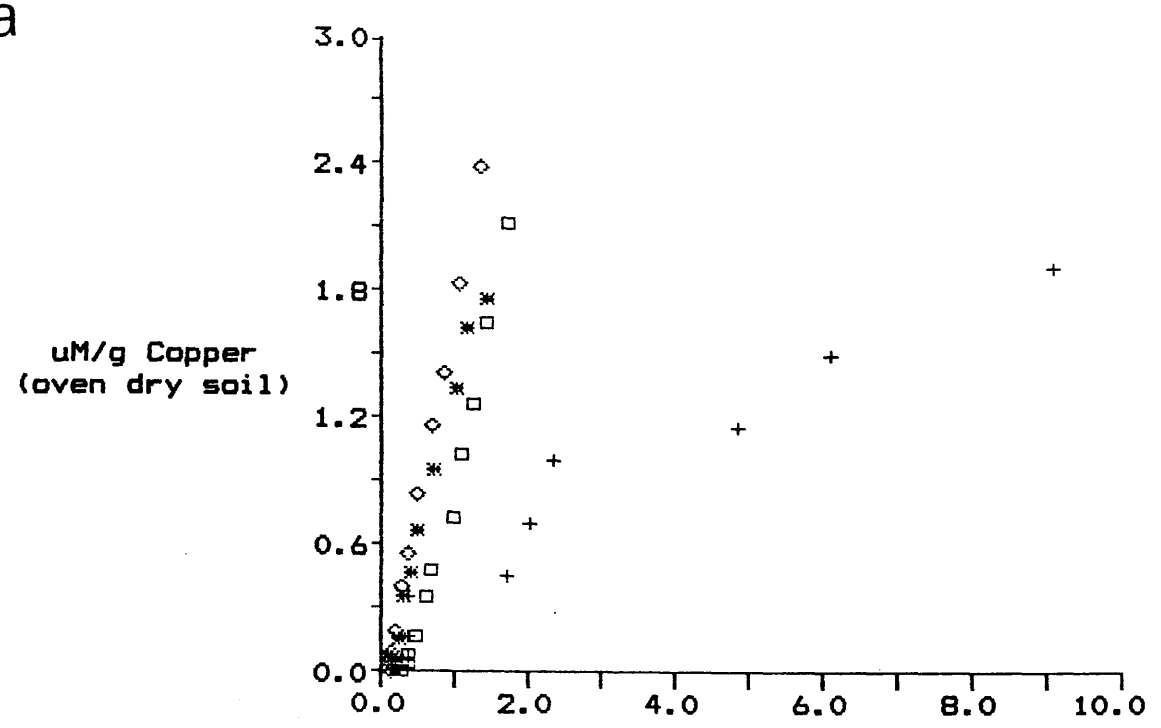
(b). BA, Dreg, FA and FS.

Expanded Lower end of Cd graph

(c). Ark, AHZ, Cap and Dun.

(d). BA, Dreg, FA and FS.

a



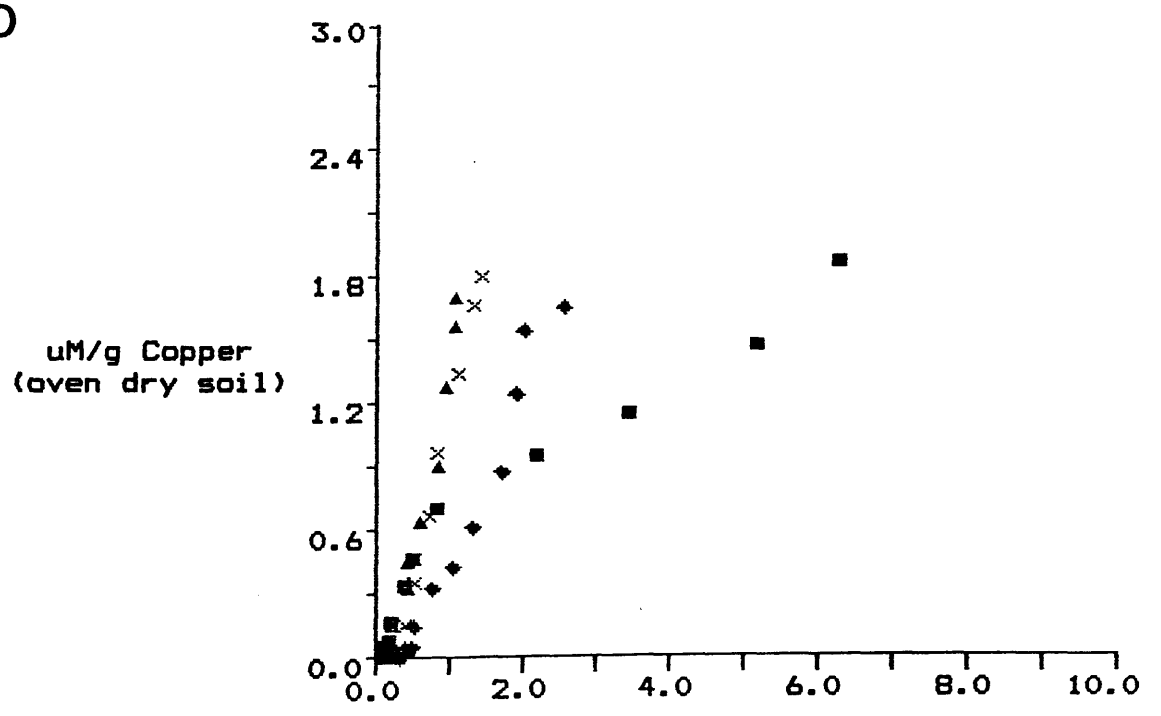
Copper uptake from 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

Cu ISE-Batch experiments.

b



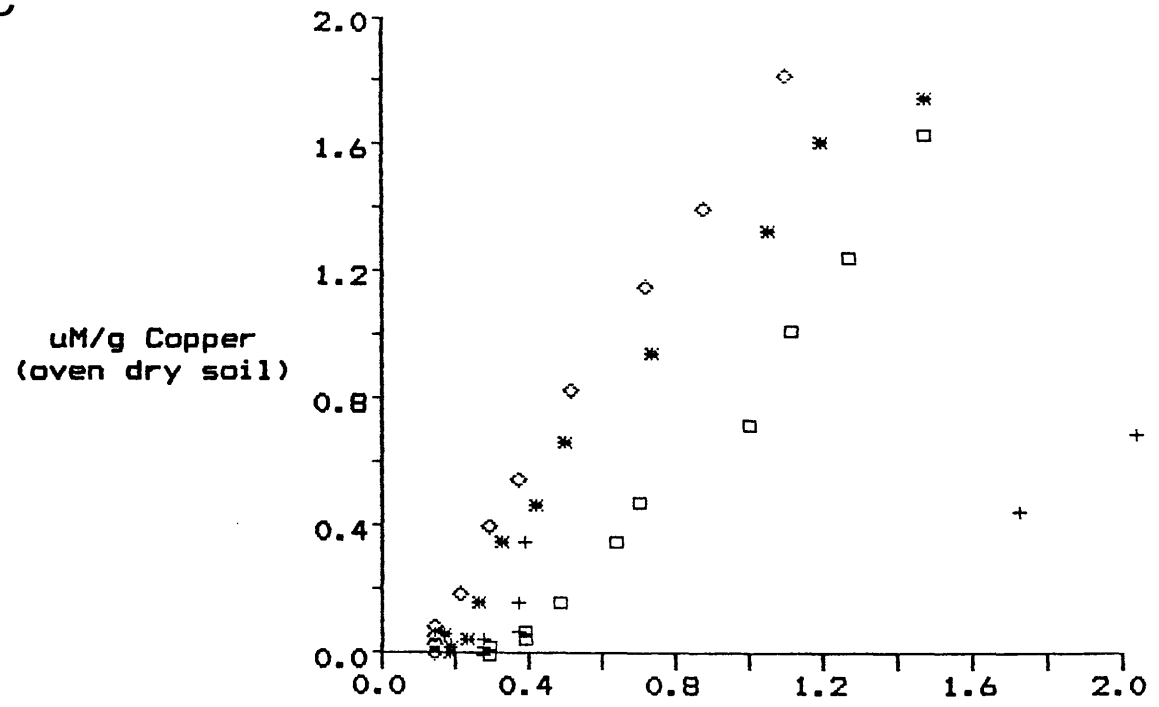
Copper uptake from 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Cu ISE-Batch experiments.

c



uM Copper at equilibrium.

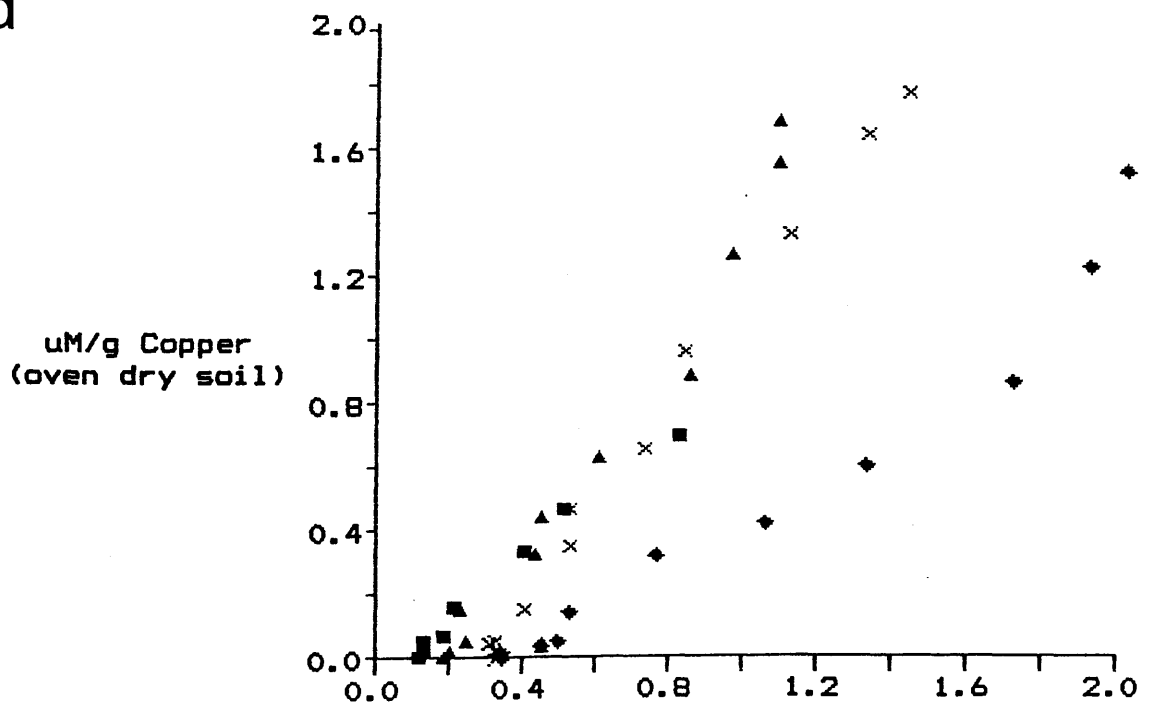
Copper uptake from 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

Cu ISE-Batch experiments.

d



uM Copper at equilibrium.

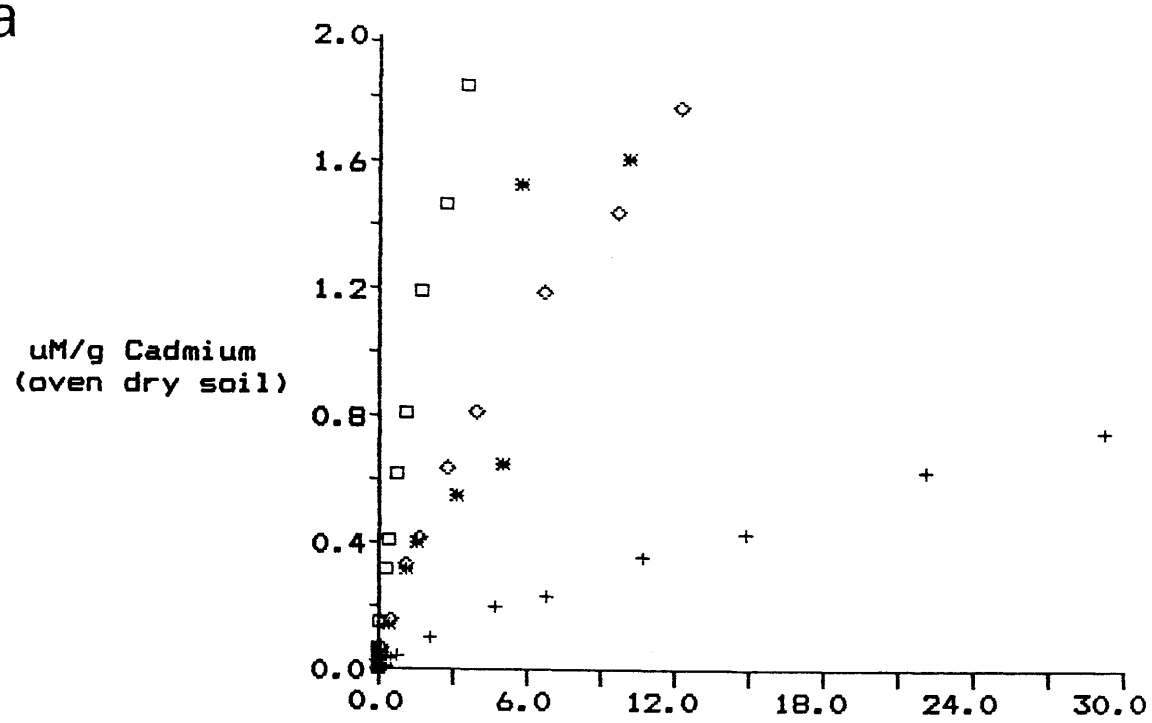
Copper uptake from 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Cu ISE-Batch experiments.

a



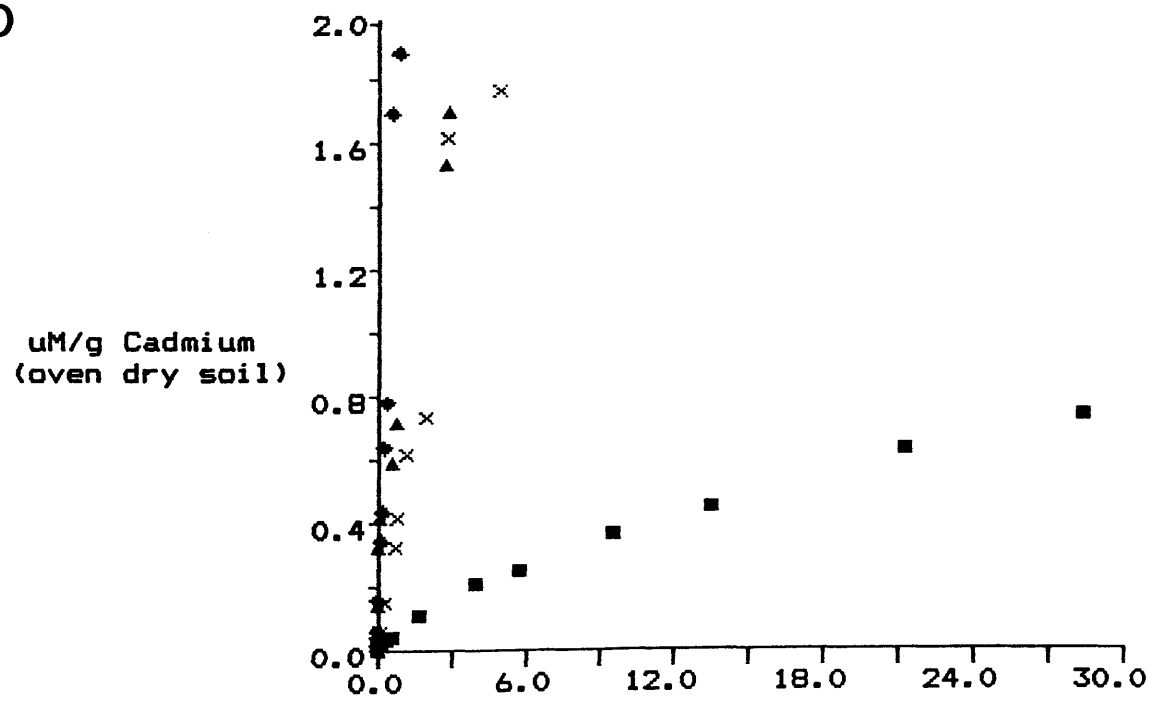
Cadmium uptake from 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

Cd ISE-Batch experiments.

b



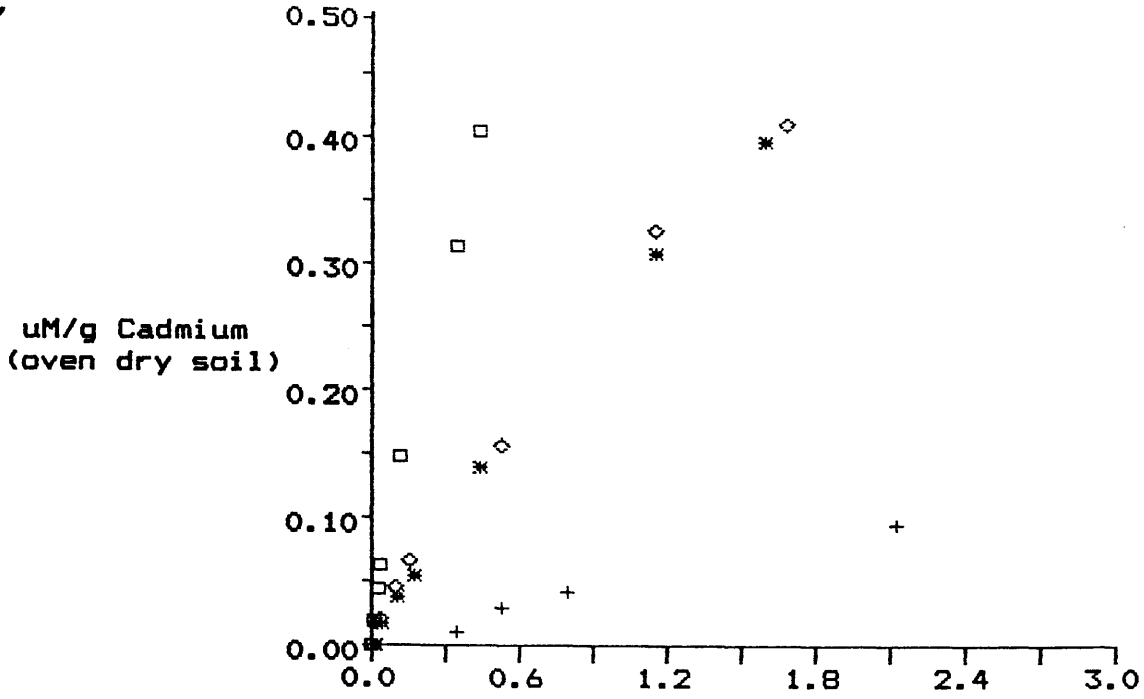
Cadmium uptake from 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Cd ISE-Batch experiments.

c



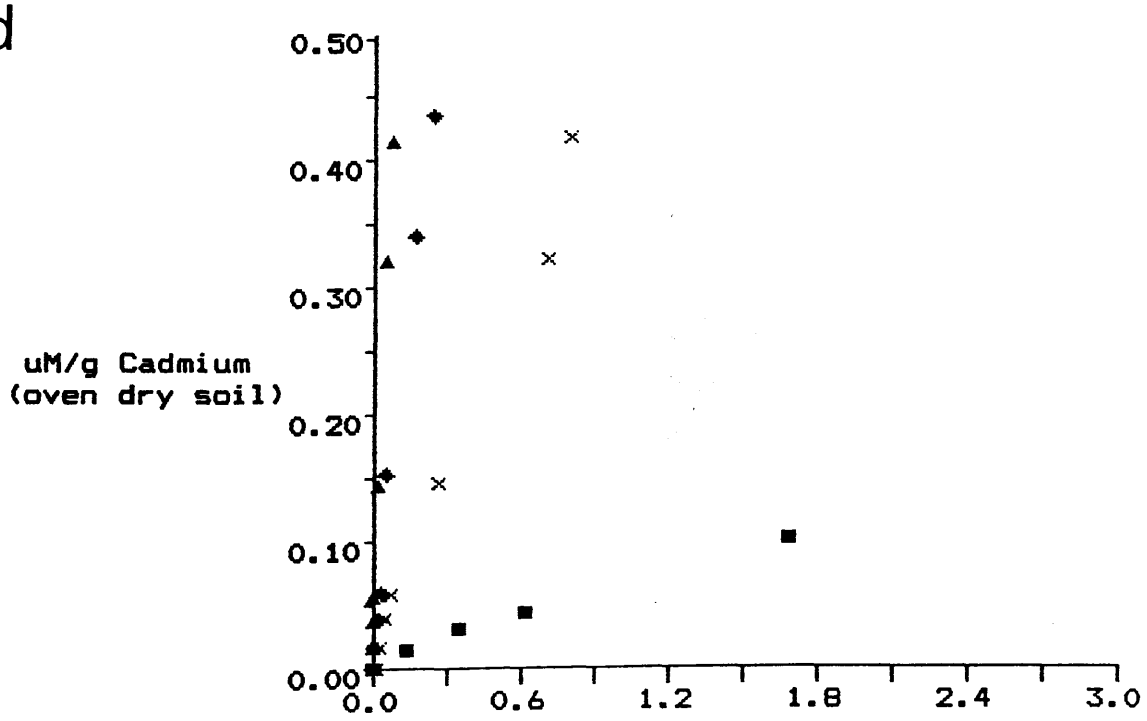
Cadmium uptake from 0.1M NaNO3.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

Cd ISE-Batch experiments.

d



Cadmium uptake from 0.1M NaNO3.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Cd ISE-Batch experiments.

Table 3.4. Isotherms: 2, lowest part of graph.

COPPER

Soil	Equation	No. points	r^2
Ark	X = 1.44C - 0.29	12	0.980
AHZ	X = 1.79C - 0.49	5	0.530
Cap	X = 1.08 - 0.34	7	0.982
Dun	X = 1.87C - 0.20	11	0.998
BA	X = 1.60C - 0.48	12	0.995
Dreg	X = 1.00C - 0.10	8	0.987
FA	X = 0.78C - 0.32	12	0.966
FS	X = 1.62C - 0.37	11	0.936

CADMIUM

Soil	Equation	No. points	r^2
Ark	X = 0.25C - 0.01	7	0.995
AHZ	X = 0.04C - 0.01	7	0.979
Cap	X = 0.88C - 0.01	7	0.993
Dun	X = 0.25C + 0.02	7	0.990
BA	X = 0.42C + 0.05	12	0.955
Dreg	X = 0.05C + 0.01	6	0.994
FA	X = 1.62C - 0.001	4	0.983
FS	X = 5.47C - 0.02	7	0.993

Turning once more to the Langmuir treatment of the data, Cu again eluded any comprehensible description by this equation (fig. 3.11. a,b). It is likely that the amounts of Cu added to the soils would be well below that required to produce site saturation. If that is so for a group of sites which have roughly similar sorption characteristics, then one of the limitations of the mechanistic application of the Langmuir isotherm has been fulfilled: Cu clearly does not conform to Langmuir's description, casting more doubt on the practice of deriving mechanisms and 'thermodynamic' constants from Langmuir data for heterogeneous surfaces. With respect to Cd, the AHZ and Dreghorn soils demonstrated the two constant Langmuir graph most clearly; such relationships were possible for all the soils and the graphs and tables are shown below; (fig. 3.12. a-c, table 3.5).

Figures 3.11. and 3.12. Langmuir Plots of Cu and Cd Sorption Data.

Figure 3.11. Langmuir Plot of Cu Data.

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

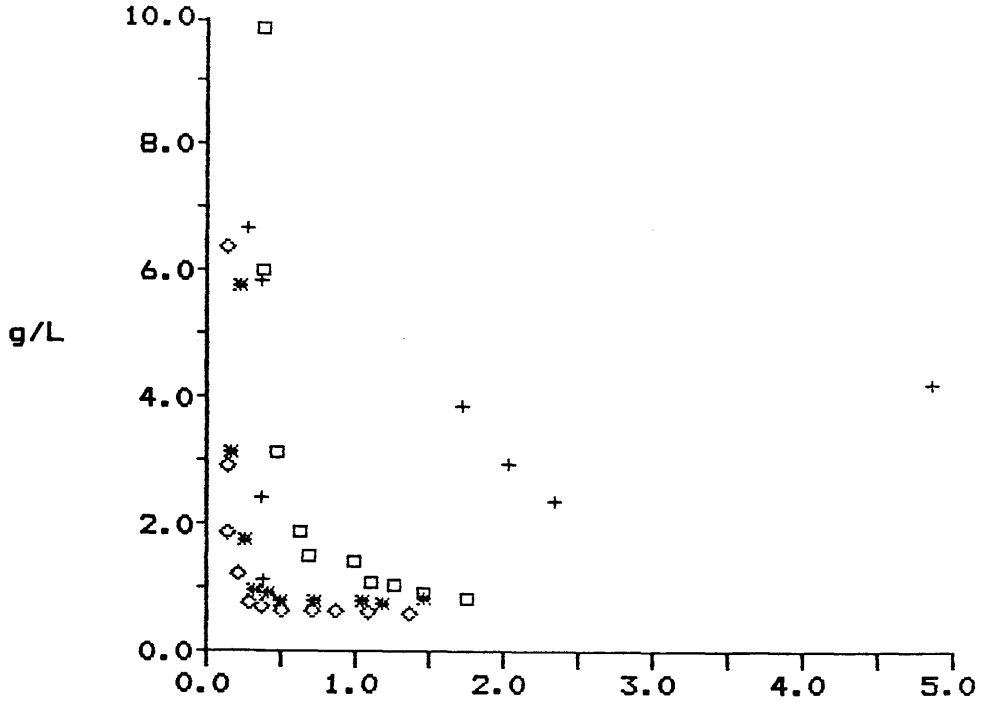
Figure 3.12. Langmuir Plot of Cd Data.

(a). Ark, Cap and Dun.

(b). BA, FA and FS.

(c). AHZ and Dreg.

a



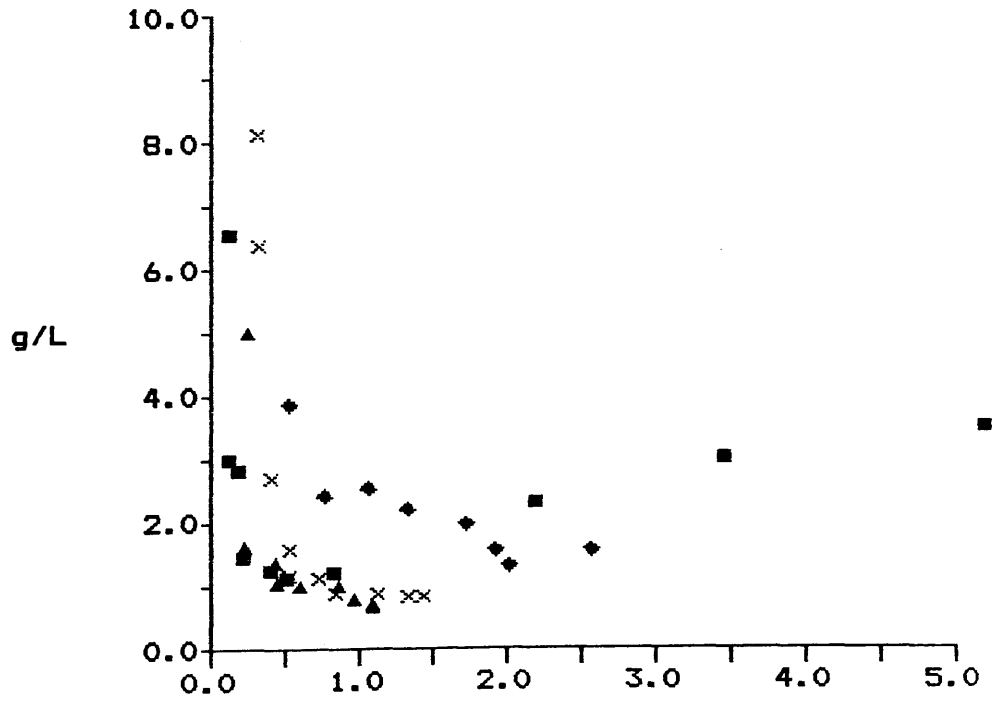
uM Copper at equilibrium.

Copper uptake in 0.1M NaNO3:Langmuir isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



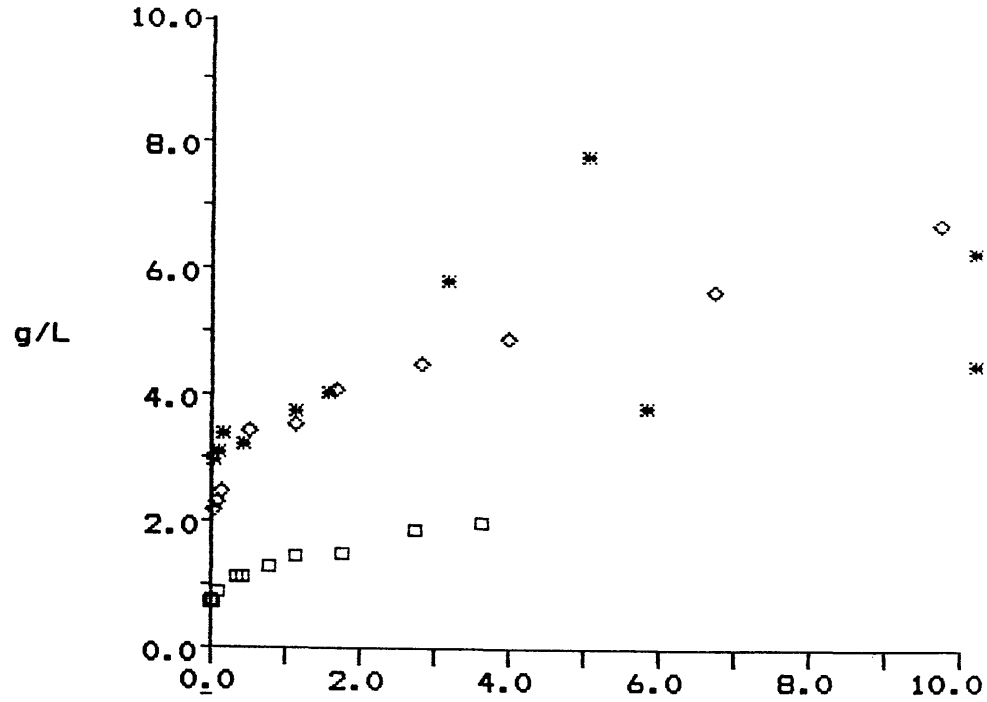
uM Copper at equilibrium.

Copper uptake in 0.1M NaNO3:Langmuir isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

a



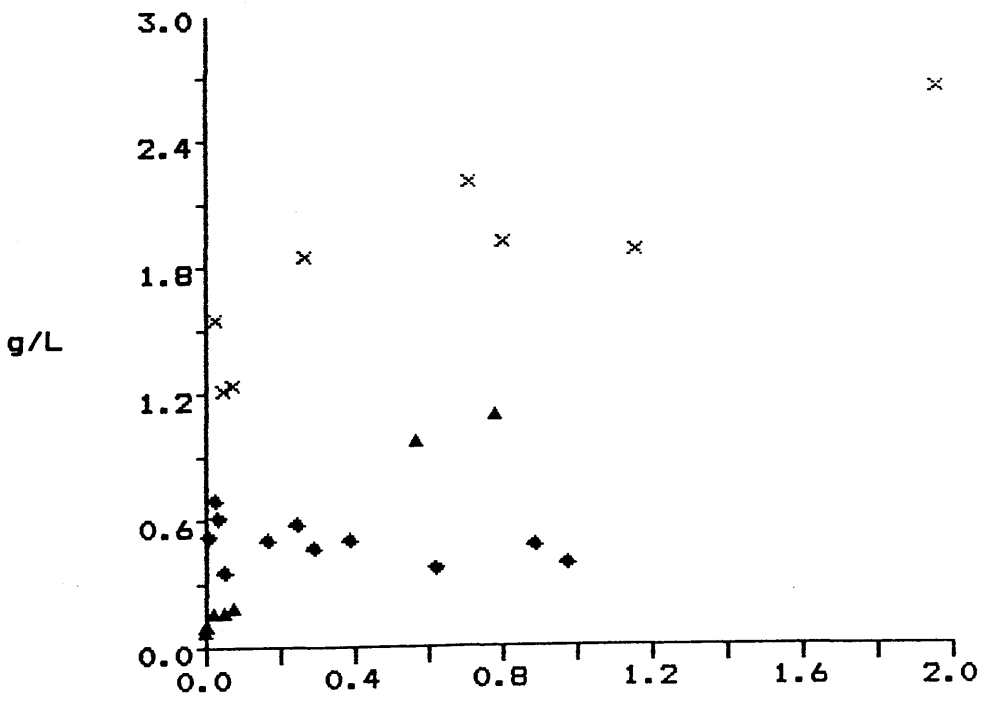
Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

ARKLESTON - * CAPRINGTON - sq.

DUNLOP - dia.

Cd ISE-Batch experiment.

b



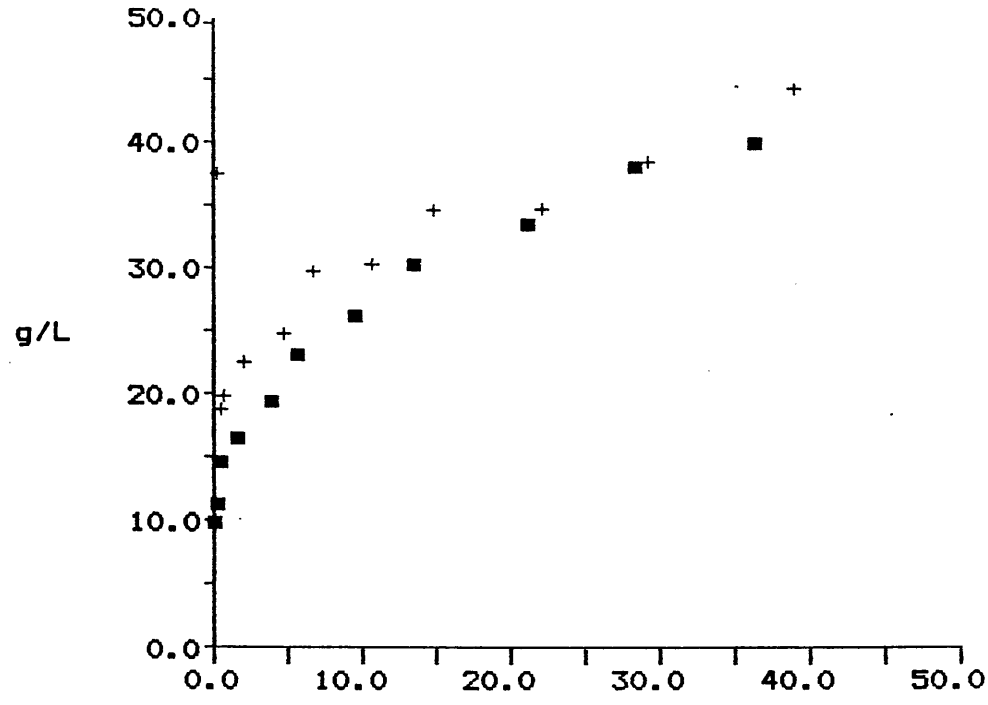
Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

BLACKSTOUN - x FEN ARABLE - dia.

FEN SUBSOIL - tri.

Cd ISE-Batch experiment.

C



Cadmium uptake in 0.1M NaNO3:Langmuir isotherm.

ARKLESTON HIGH ZINC - + DREGHORN - sq.

Cd ISE-Batch experiment.

Table 3.5. Isotherms: 2, Two-Constant Langmuir examples for Cadmium.

Arkleston	K_1 = 0.329	K_2 = 0.010
	X_1m = 1.062	X_2m = 20.236
Arkleston High Zinc	K_1 = 0.055	K_2 = 0.017
	X_1m = 0.928	X_2m = 2.260
Caprington	K_1 = 0.871	K_2 = 0.221
	X_1m = 1.522	X_2m = 4.052
Dunlop	K_1 = 0.483	K_2 = 0.075
	X_1m = 0.899	X_2m = 3.571
Blackstoun Alluvial	K_1 = 0.999	K_2 = 0.047
	X_1m = 0.761	X_2m = 10.858
Dreghorn	K_1 = 0.399	K_2 = 0.026
	X_1m = 0.247	X_2m = 1.796
Fen Subsoil	K_1 = 14.235	K_2 = 0.416
	X_1m = 0.734	X_2m = 2.986

As in the previous section, the best description of the Cd sorption data could be achieved using the van Bemmelen-Freundlich equation, the results of which are shown in figure 3.13 a,b. The gradients of all these lines were less than 1, as befits use of the equation (see Table 3.6.).

Table 3.6. Isotherms: 2, Freundlich.

COPPER

Soil	Low Equation	r^2	High equation	r^2
Ark	logX = 3.80logC + 1.26	0.694	logX = 1.10logC + 0.10	0.985
AHZ	logX = 5.95logC + 1.68	0.728	logX = 0.57logC + 0.30	0.884
Cap	logX = 3.88logC + 0.30	0.976	logX = 1.77logC - 0.10	0.984
Dun	logX = 3.19logC + 1.30	0.833	logX = 1.15logC + 0.22	0.997
BA	logX = 5.22logC + 1.05	0.839	logX = 1.39logC + 0.04	0.987
Dreg	logX = 2.03logC + 0.31	0.917	logX = 0.49logC - 0.17	0.966
FA	logX = 4.32logC + 0.06	0.930	logX = 1.60logC - 0.39	0.978
FS	logX = 3.28logC + 0.75	0.770	logX = 1.54logC - 0.12	0.985

CADMIUM

Soil	Low Equation	r^2
Ark	logX = 0.92logC - 0.57	0.999
AHZ	logX = 0.89logC - 1.39	0.979
Cap	logX = 0.81logC - 0.15	0.997
Dun	logX = 0.79logC - 0.58	0.998
BA	logX = 0.88logC - 0.30	0.991
Dreg	logX = 0.74logC - 1.18	0.998
FA	logX = 1.62logC - 0.001	0.983
FS	logX = 0.56logC - 0.02	0.968

If the two sets of isotherm data for Cd are combined, van Bemmelen-Freundlich straight lines are obtained; the equations for these are listed below (table 3.7, figure 3.14 a,b), and are comparable to the individual ones.

Table 3.7. Combined logarithmic equations for Cd.

soil	equation	r^2
Ark	logX = 0.75logC - 0.63	0.969
AHZ	logX = 0.83logC - 1.31	0.970
Cap	logX = 0.68logC - 0.29	0.973
Dun	logX = 0.74logC - 0.57	0.991
BA	logX = 0.81logC - 0.30	0.988
Dreg	logX = 0.70logC - 1.16	0.993
FA	logX = 0.88logC + 0.18	0.974
FS	logX = 0.63logC + 0.18	0.962

Figures 3.13. and 3.14. Freundlich Plots of Cd and Combined-Cd Sorption Data.

Figure 3.13. Freundlich Plot of Cd Data.

(a). Ark, AHZ, Cap and Dun.

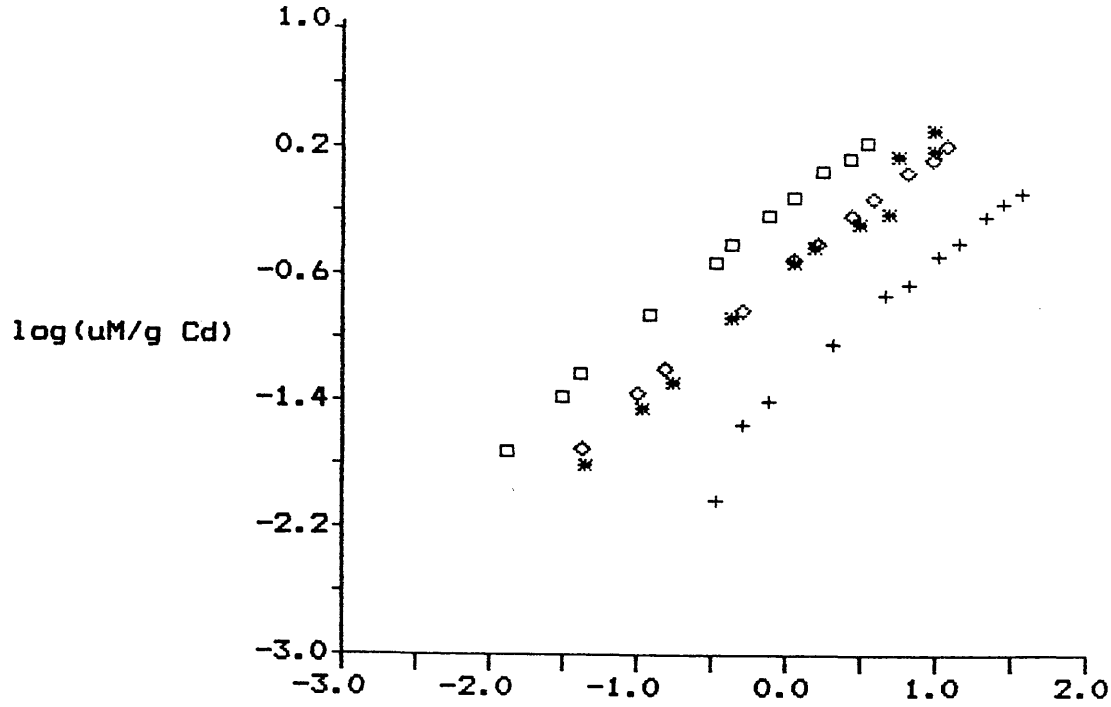
(b). BA, Dreg, FA and FS.

Figure 3.14. Freundlich Plot of Combined Cd Data.

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

a



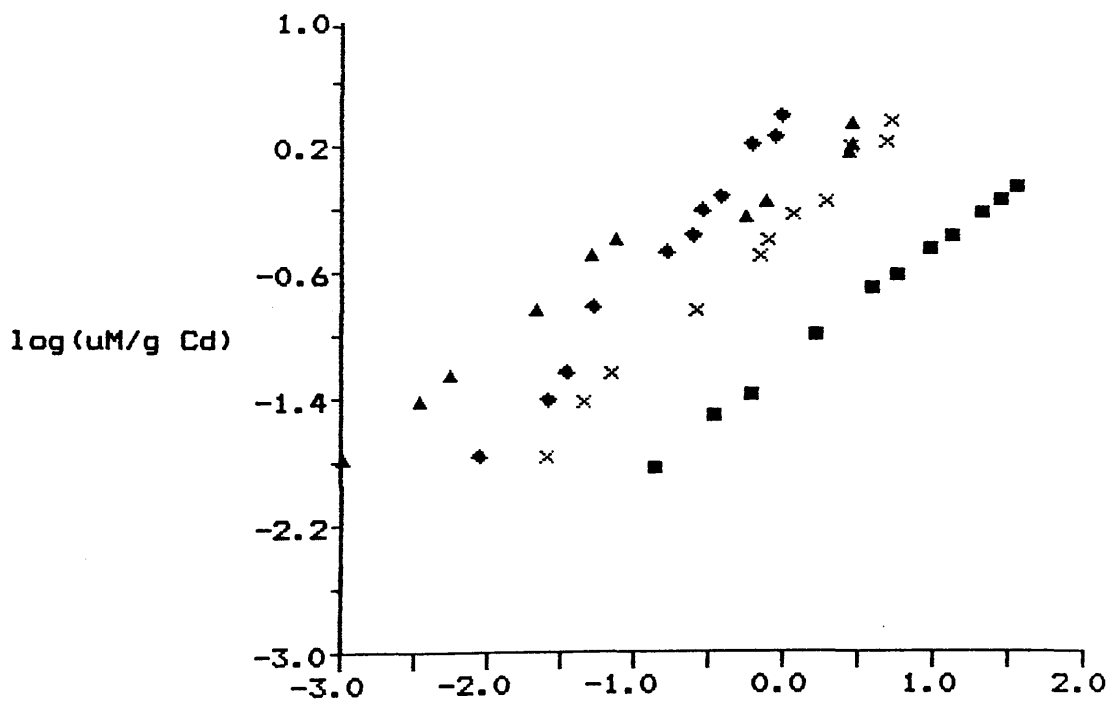
Cadmium uptake in 0.1M NaNO3:Freundlich isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

Cd ISE experiments

b

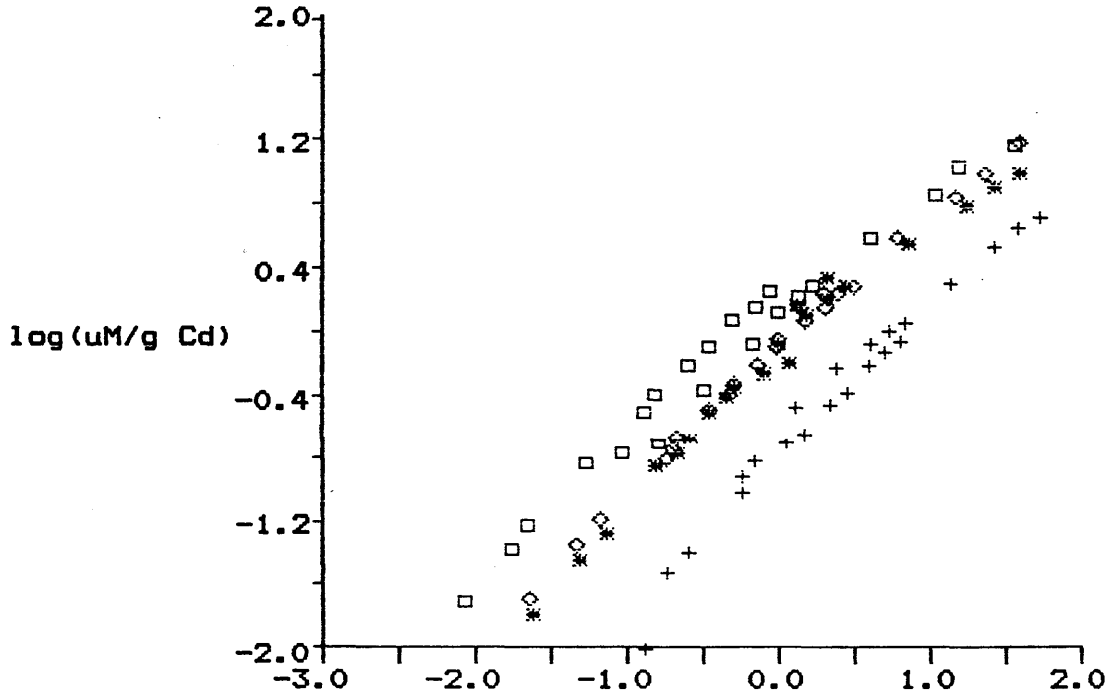


Cadmium uptake in 0.1M NaNO3:Freundlich isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

a

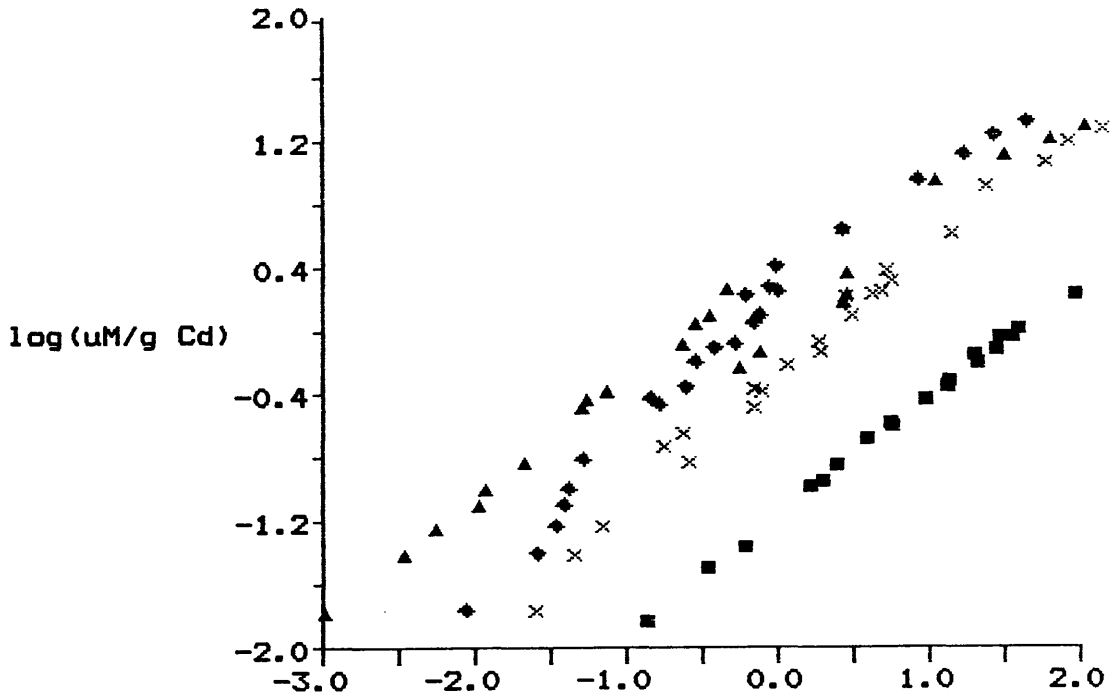


Cadmium uptake in 0.1M NaNO3:Freundlich isotherm.
(combined results)

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

b



Cadmium uptake in 0.1M NaNO3:Freundlich isotherm.
(combined results)

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

In general, the low level isotherm had a higher gradient than the high level one. Combining the results gave an average gradient which describes the soil-Cd interaction well over 5 orders of magnitude of equilibrium concentrations: against any criterion, this must be viewed as a useful tool in the estimation of soil Cd levels.

In the absence of any simple mathematical description of Cu sorption, an effort was made to fit polynomial lines to the data; whilst this met with some degree of success, 2-order polynomials yielding good r values, for most of the data sets (table 3.8.). The two data sets (from sections 3.3.1.1. and 3.3.1.2.), in terms of the equations of the graphs, seem quite independent, and the two-constant Freundlich (figure 3.15. a,b) must be viewed as being the simplest means of summarizing Cu sorption data.

Table 3.8. Polynomial Regression lines for Cu C v X.

soil	equation	r
Ark1	$X = -0.04 + 0.23C - 6.48x10^{-4}C^2$	0.98
Ark2	$X = -0.38 + 2.22C - 0.51C^2$	1.00
AHZ2	$X = 0.03 + 0.33C - 0.01C^2$	0.98
Cap1	$X = 0.10 + 0.81C - 0.01C^2$	0.99
Cap2	$X = -0.26 + 0.68C + 0.38C^2$	1.00
Dun1	$X = 0.45 + 0.83C + 0.01C^2$	0.99
Dun2	$X = -0.23 + 1.99C + 0.09C^2$	1.00
BA1	$X = -0.81 + 1.51C - 0.02C^2$	1.00
BA2	$X = -0.55 + 1.85C - 0.15C^2$	1.00
Dreg1	$X = 0.94 + 0.09C - 1.41x10^{-4}C^2$	0.99
FA1	$X = 0.50 - 0.29C - 0.02C^2 + 0.02C^3$	1.00
FA2	$X = 0.10 - 0.47C + 0.93C^2 - 0.20C^3$	0.99
FS1	$X= -49.78+ 65.74C- 27.94C^2+ 3.95C^3$	0.98
FS2	$X = -0.02 + 0.07C + 1.28C^2$	0.98

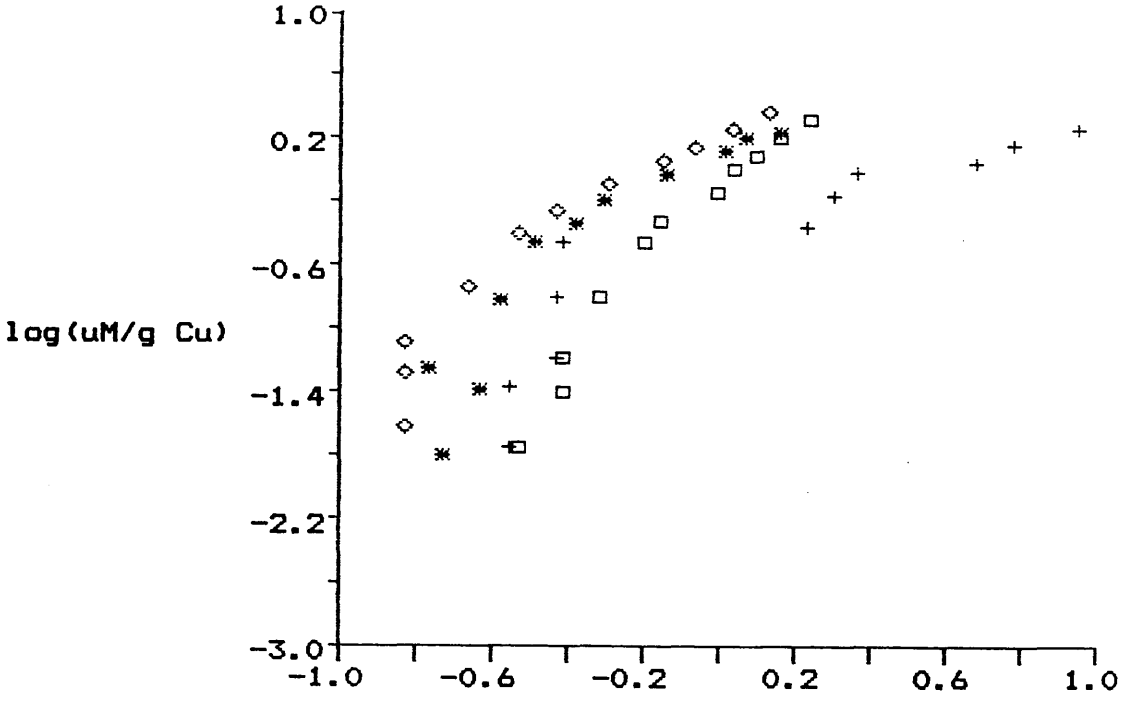
note; 1 refers to the Batch data, 2 to the ISE-Batch data.

Figure 3.15. Freundlich Plot of Cu Data.

(a). Ark, AHZ, Cap and Dun.

(b). BA, Dreg, FA and FS.

a



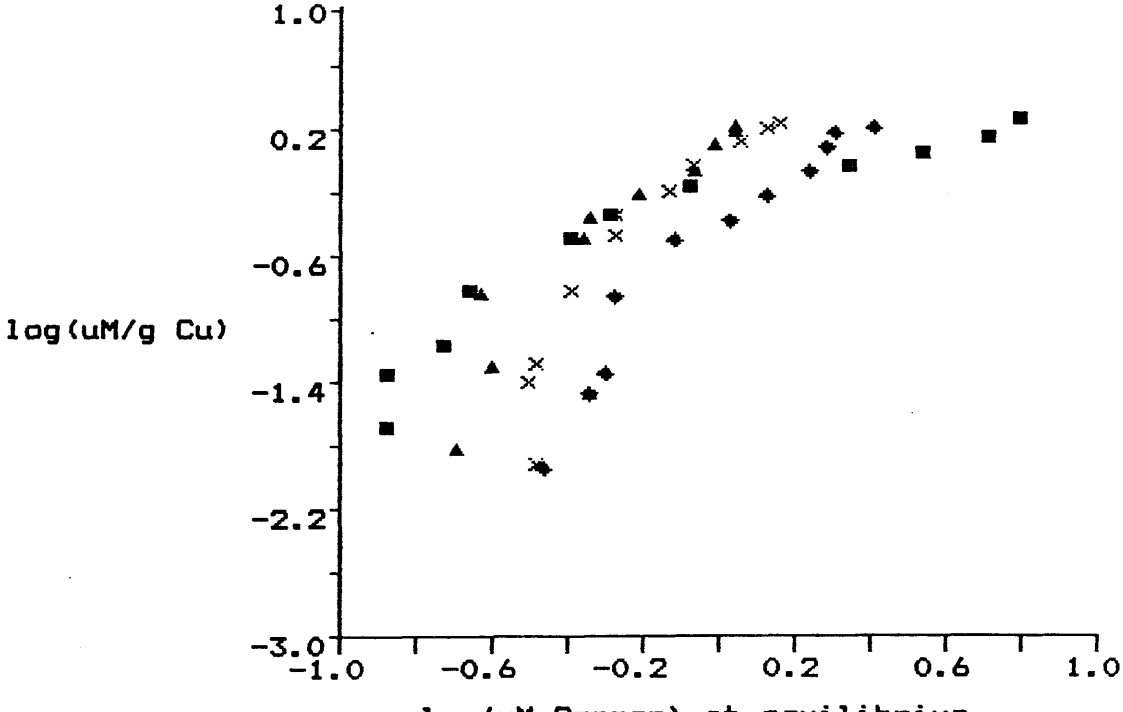
Copper uptake in 0.1M NaNO3:Freundlich isotherm.

ARKLESTON - * ARKLESTON HIGH ZINC - +

CAPRINGTON - sq. DUNLOP - dia.

Cu ISE-Batch experiments

b



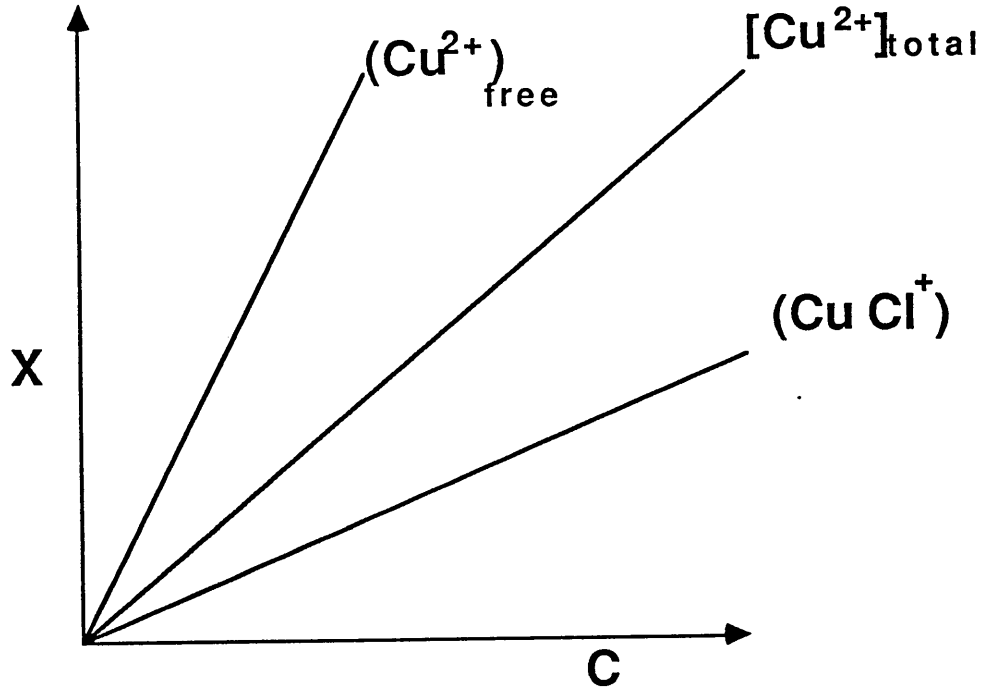
Copper uptake in 0.1M NaNO3:Freundlich isotherm.

BLACKSTOUN - x DREGHORN - sq.

FEN ARABLE - dia. FEN SUBSOIL - tri.

Cu ISE-Batch experiments

The sorption isotherms constructed via the AAS measurements were obtained from measurements of the total metal in solution. This relationship represents a sort of average of the various sorbing species of Cu and Cd. However, it is likely that the various solution species are sorbed to different extents; if it was possible to measure independently the disappearance of each species from solution, then a C v X diagram like the one below may be constructed;



In the latter set of isotherms (section 3.3.1.2., the activity of Cu^{2+} and Cd^{2+} was determined by ISE's, both in the suspensions and the supernatants of the equilibrated systems.

The cadmium ISE measurements in both suspension and supernatant, despite the electrode's good response in pure standard solutions, have had to be discarded in this part of the work. In all instances, the measured Cd^{2+} activity was higher than the concentration measured in solution (by 9

orders of magnitude in some instances!). Activity coefficients greater than one can be discounted, as these are encountered only in the formation of solid solutions (Stumm and Morgan 1981) (which would necessitate the presence of the particles on which the cadmium solid-solution was forming to be in very close proximity to the electrode membrane - it is thought unlikely that there would be sufficient numbers of such species to exert the sort of influence recorded). Gross changes in the ionic strength of the background electrolyte due to sorption have also been ruled out.

The pH changes on filtering were of the same order of magnitude as witnessed in the Cu experiments;

Caprington (0μM Cd added);

$pH_{suspension}$ 5.98

$pH_{supernatant}$ 5.74

As mentioned in section 2.2.2., millimolar levels of Ca^{2+}, Mg^{2+} and Al^{3+} as well as micromolar levels of Cu^{2+} will interfere with the response of the Cd electrode - by membrane poisoning. Thus it may be concluded that the 24h.shaking period resulted in these ions being released from the soil to such a degree that the electrode performance is vastly impaired (*cf.* Genklene solution extract figures, table 2.3., bearing in mind that these appeared to underestimate the cation levels). This has to be seen as being very unfortunate as one of the basic ideas behind the use of the electrodes was their ability to demonstrate the relative dependence of solution Cd and Cu levels on organic and inorganic components in solution.

The copper results can be considered and compared to results of activity obtained by calculation (*cf* nitrate speciation program in appendix 1). Moving from low to high

concentrations, there was little change in the pH of either the suspensions or the supernatants, which, when transferred to speciation calculations translates simply to the multiplication of the measured concentration by a constant factor: an activity coefficient. Thus it would be expected that the C v X isotherms based on calculated activities should simply reflect the concentration-based isotherm, but with a steeper gradient. When the data are applied to van Bemmelen-Freundlich treatment, the gradient of the graph should be maintained, but the intercept altered. If the speciation programme is describing the solution composition adequately, then the isotherm points obtained by calculation should coincide with those measured by the electrode. The results of this approach are summarized in figure 3.16.(a-h) for Cu and figure 3.17.(a-h) for Cd, demonstrating the C v X relationship (where a symbol is referred to on the axis label but does not appear on the graph, this is due to overlap of the points, mainly where the calculated activity figures are concerned). Figures 3.18.(a-h) and 3.19.(a-h) show the data under van Bemmelen-Freundlich treatment for Cu and Cd respectively.

Many of the soils gave Cu ISE figures which lay below the linear portion of the calibration graph which was used, but the figures are still presented here for the purpose of comparison. As predicted above, the C v X graphs demonstrate increased gradients when only 'free' Cu^{2+} and Cd^{2+} in solution are considered, indicating that the soil affinity for the free ion is far greater than the average for all Cu and Cd species: this is quite conclusively shown by the Cu ISE figures. For Cd assumptions can be made only from the calculated figures, but there is no reason to suppose greatly different behaviour. A noticeable feature for Cu is the presence in four of the graphs of ISE points

which appear to lie upon the y-axis of the C v X graph. Interestingly, three of these four soils were the only ones which yielded detectable figures for soluble organic matter. If the van Bemmelen-Freundlich plots are considered, the data points are pulled apart slightly and allow more of a comparison to be drawn.

If two extremes are considered: a soil with a very high level of total organic matter and a soil with a very low level of total organic matter, then it may, with good reason, be assumed that the latter soil will contribute less soluble organic matter than the former. If the pH of the soils is also taken into account, this interpretation must be altered - the higher the pH of the soil, the greater will be the tendency for the inorganic surfaces and the organic materials to repel one another, thereby releasing more organic material into solution.

In 0.1M $NaNO_3$ the pH range of the 8 soils follows the sequence;

FS > FA > Cap > Ark > BA > Dun > AHZ > Dreg.

Whilst the Tinsley organic matter contents follow this sequence;

BA > Cap > Dun > AHZ > FA > Ark > FS > Dreg.

Given this information, it might be expected that the soluble organic matter would play a role in the behaviour of the two Fen soils, BA, Cap and Dun. On the logarithmic Cu isotherms, there is a considerable gap between the calculated and measured lines for the above mentioned 5 soils, the more acid (Ark, Dreg and AHZ) tending to cluster together to a greater degree. Given the fact that the calculated figures are based upon a calculation which makes no attempt to account for organic interactions, the gulf between the calculated and the ISE figures must reflect the

relative importance of soluble organic matter in the chemical interactions of these soils: The measured activity coefficients found are quite a bit smaller than those predicted by calculation, ie.

For $M^{2+,-}$ ions.

	Calculated activity coefficient	Measured activity coefficient
FA	0.016	1.42×10^{-5}
Dreg	0.332	0.170

As mentioned in section 1.2.3., the speciation of Cd is relatively pH insensitive: hence, despite differences in the supernatant and suspension pH's, the calculated points show such small differences that they lie almost on top of one another. The resultant graphs are much as would be expected from the discussion of the effect of a constant factor on one set of data points.

Figures 3.16. and 3.17. Cu and Cd AAS, ISE and Calculated Activity Sorption Isotherms.

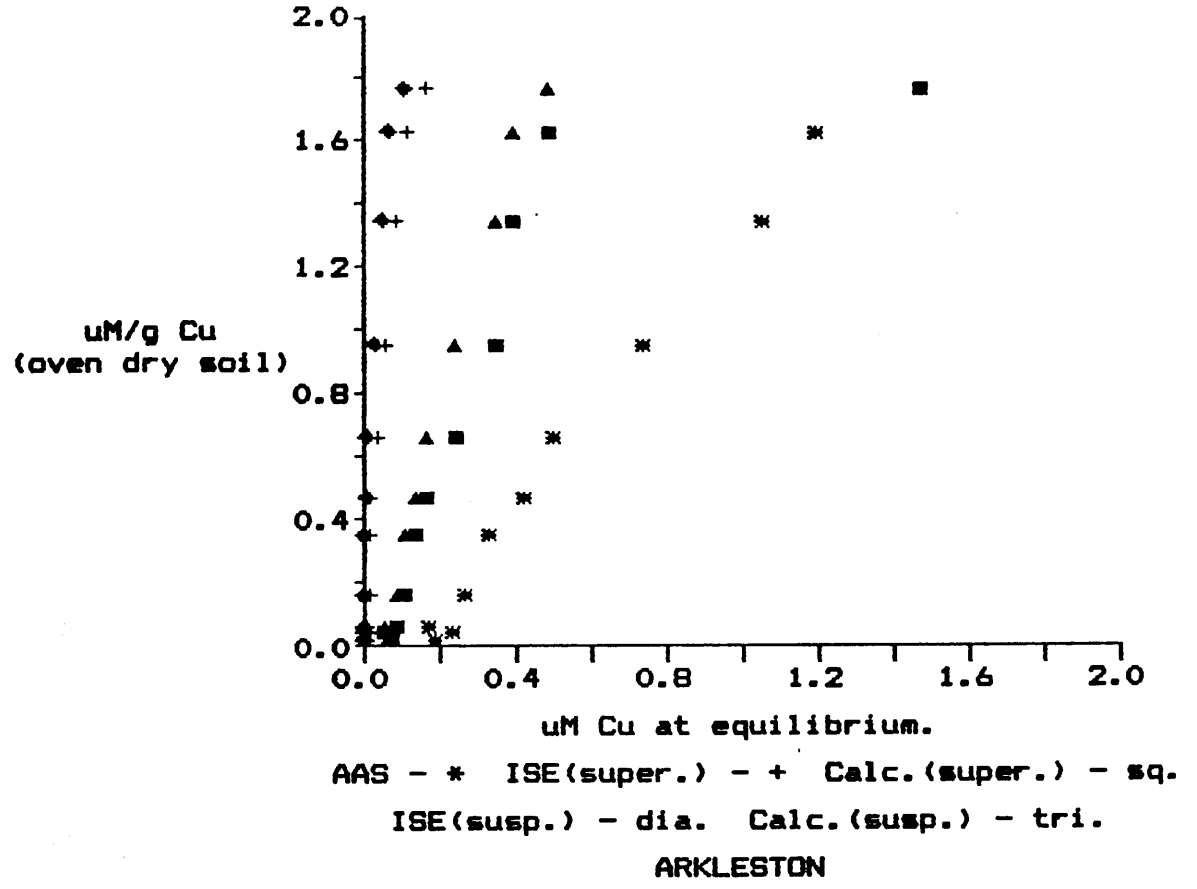
Figure 3.16. Cu AAS, ISE and Calculated Activity Sorption Isotherms.

(a). Ark.
(b). AHZ.
(c). Cap.
(d). Dun.
(e). BA.
(f). Dreg.
(g). FA.
(h). FS.

Figure 3.17. Cd AAS, ISE and Calculated Activity Sorption Isotherms.

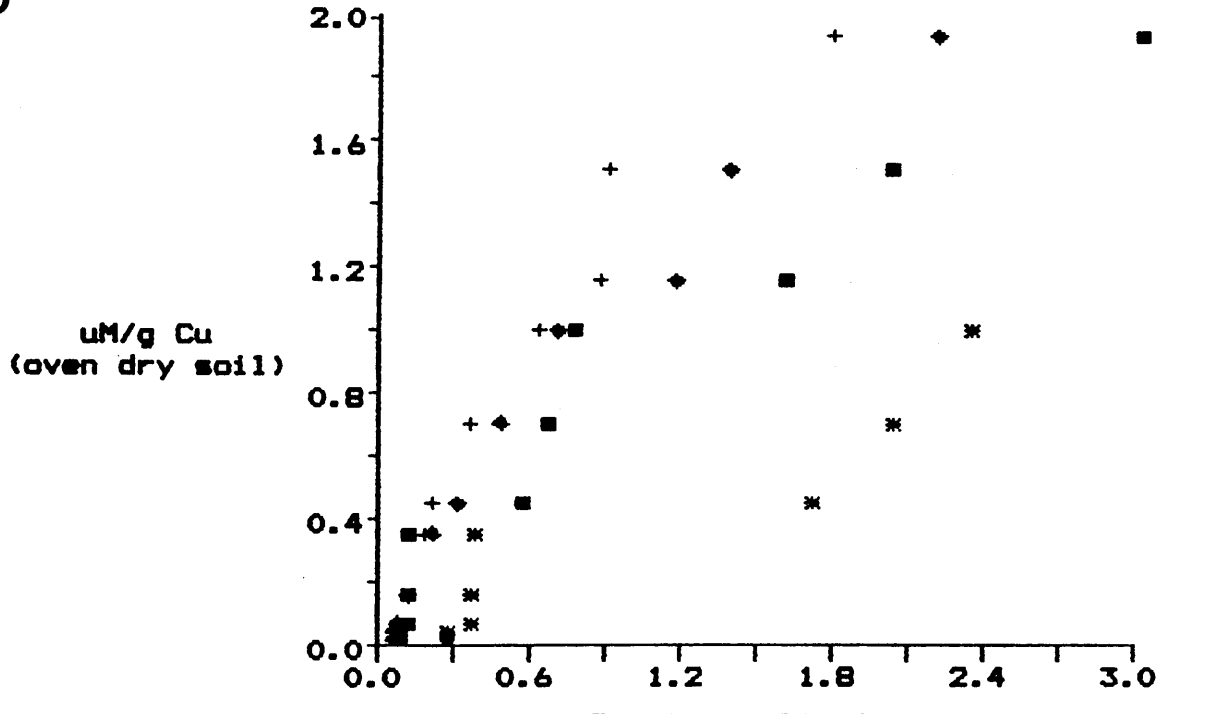
(a). Ark.
(b). AHZ.
(c). Cap.
(d). Dun.
(e). BA.
(f). Dreg.
(g). FA.
(h). FS.

a



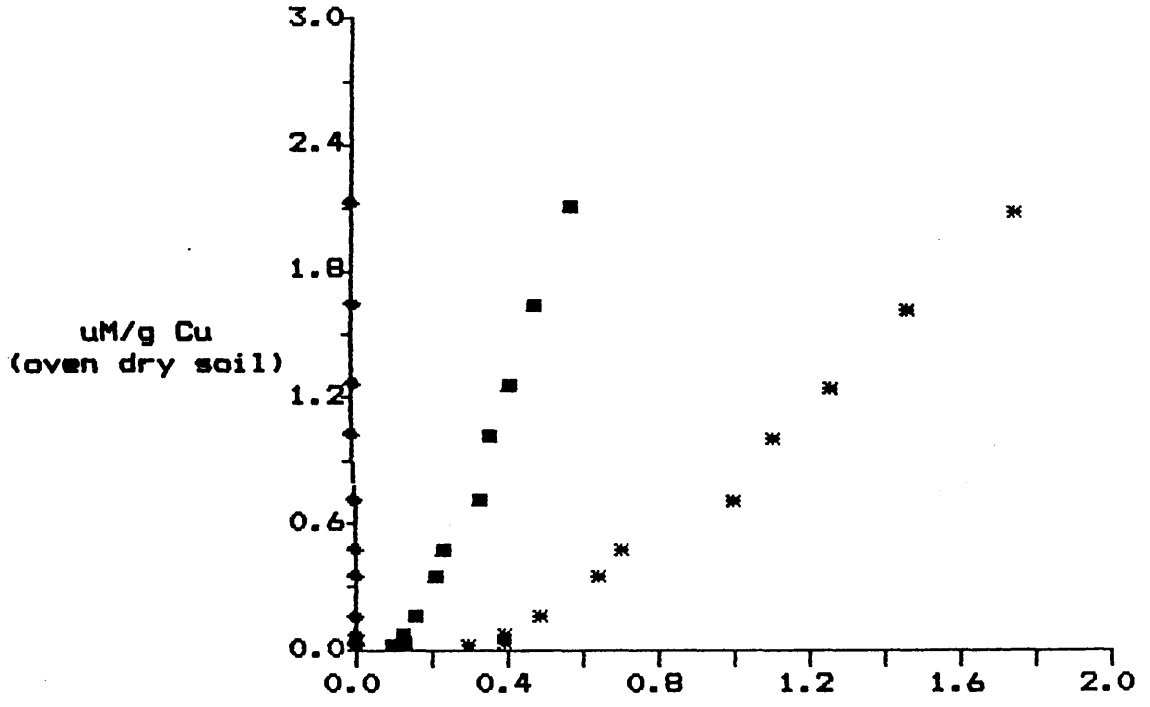
AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
ARKLESTON

b



AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
ARKLESTON HIGH ZINC

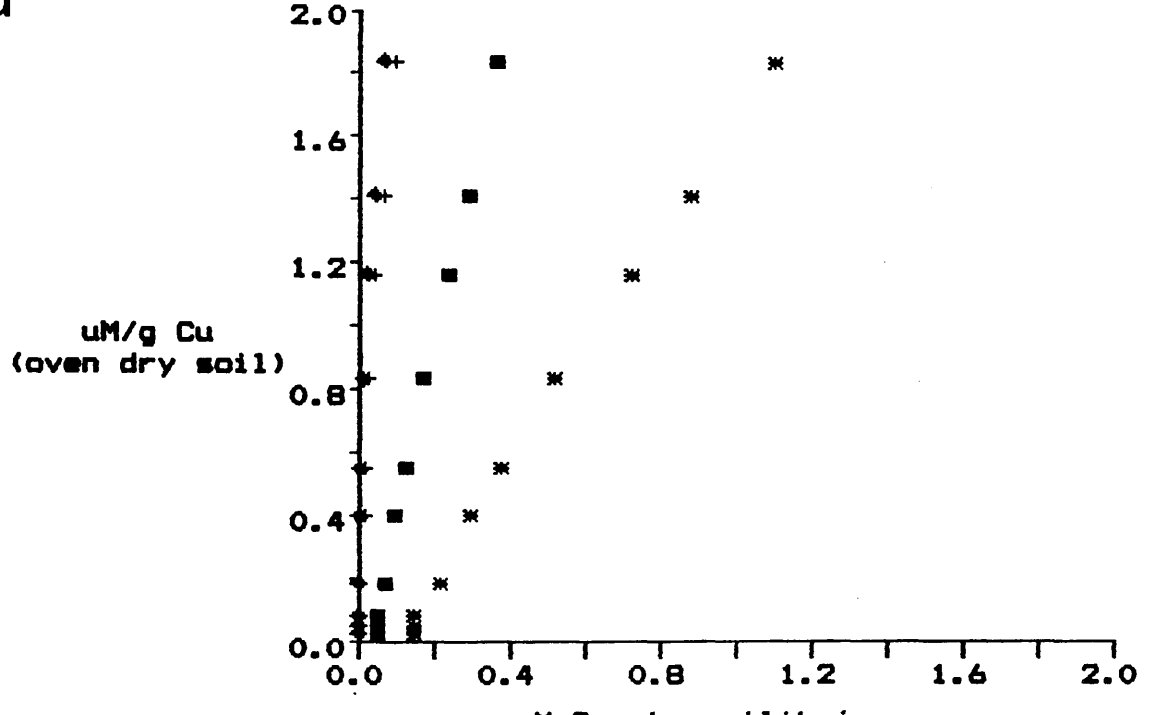
c



AAS - * ISE(super.) - + Calc.(super) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.

CAPRINGTON

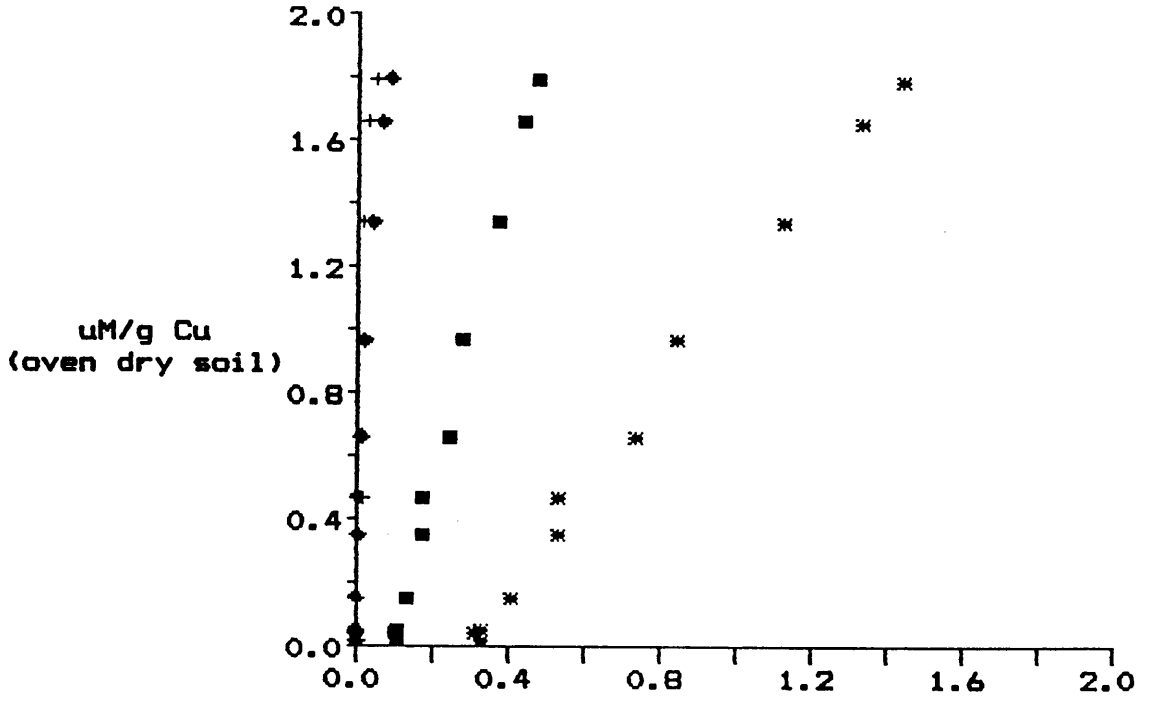
d



AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.

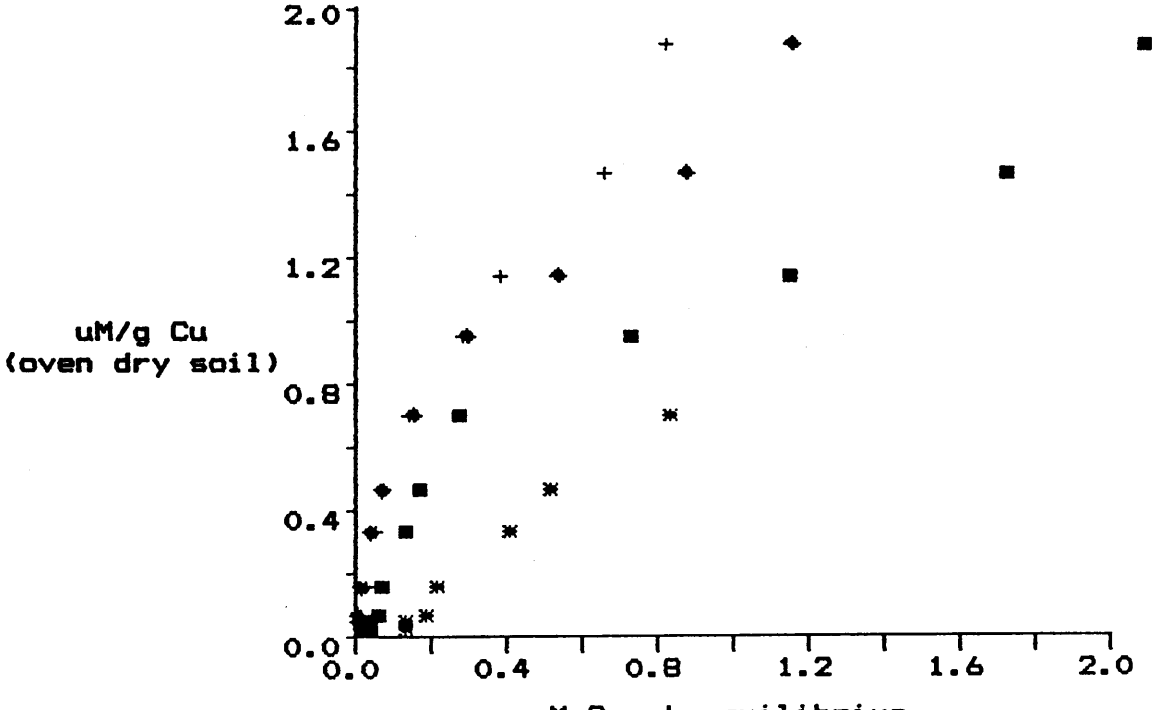
DUNLOP

e



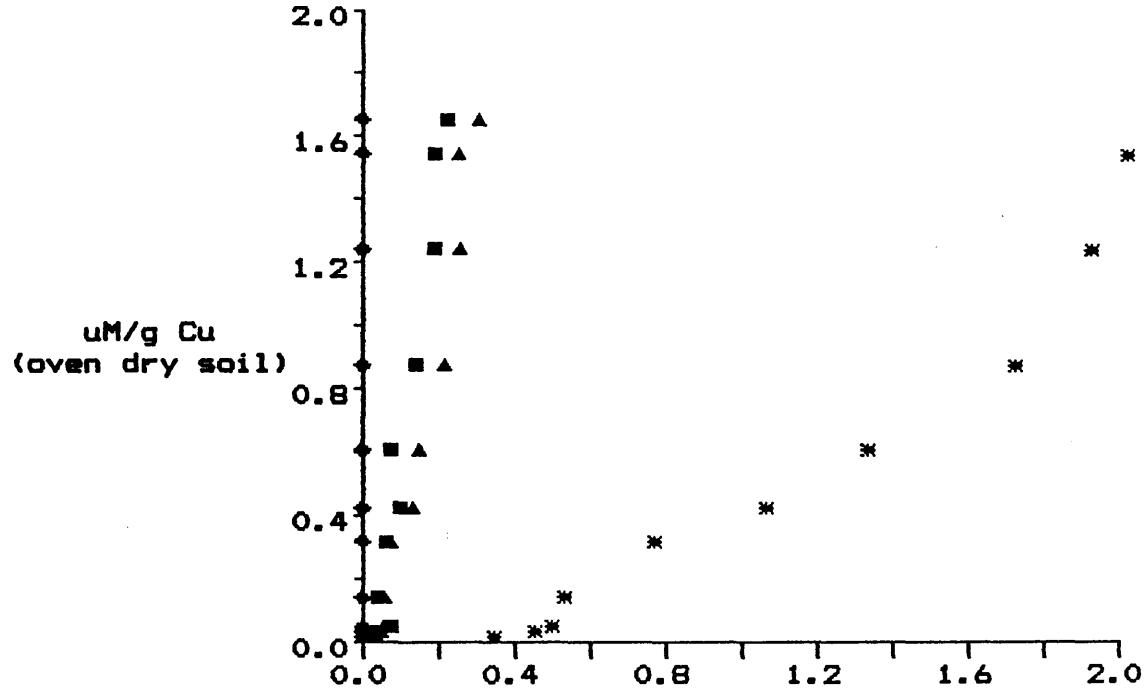
AAS - * ISE(super.) - + Calc.(super) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
BLACKSTOUN ALLUVIAL

f



AAS - * ISE(super.) - + Calc.(super) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
DREGHORN

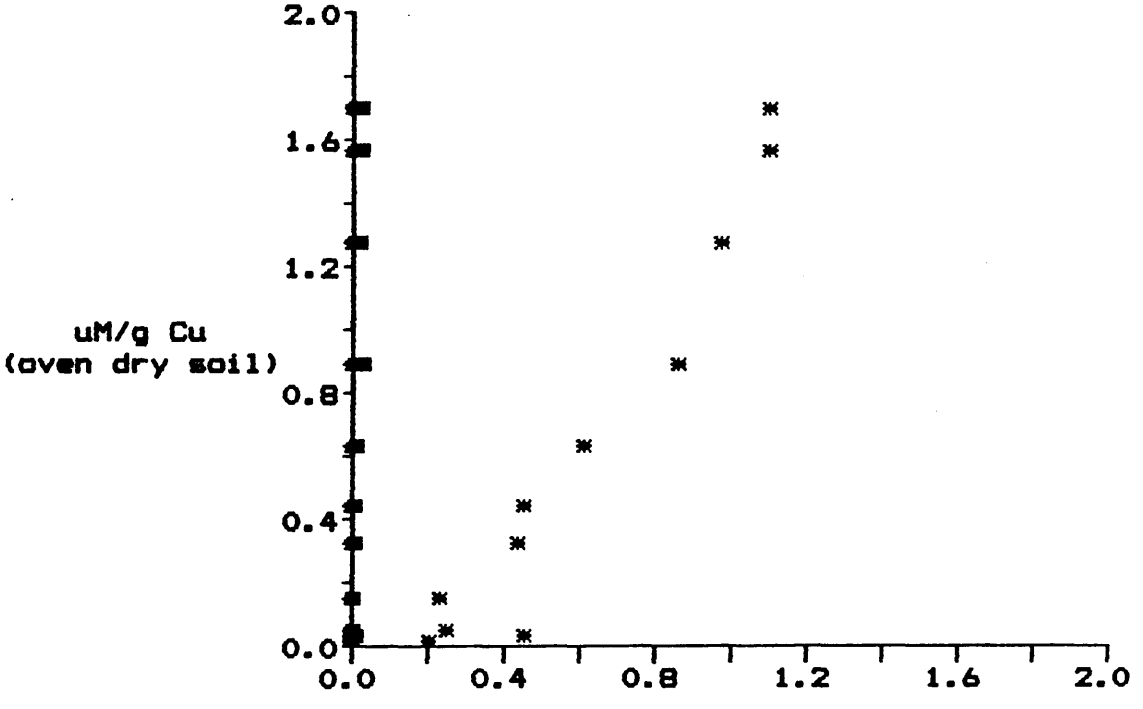
g



AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.

FEN ARABLE

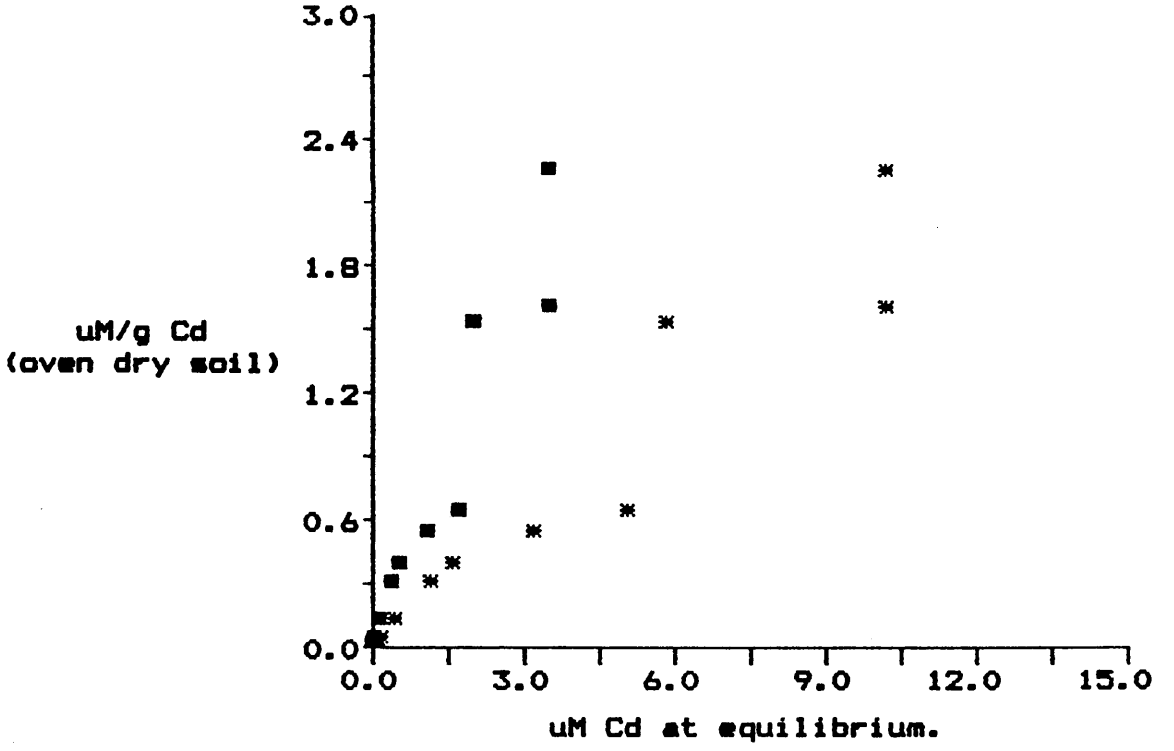
h



AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.

FEN SUBSOIL

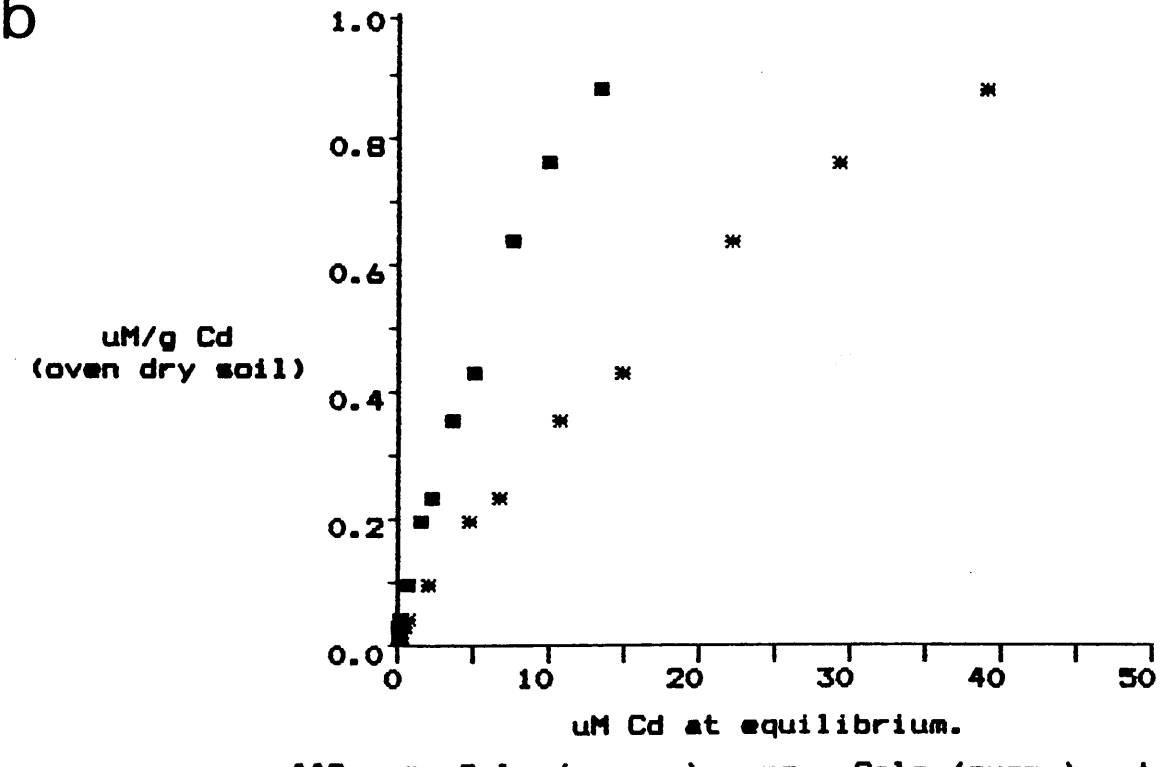
a



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

ARKLESTON

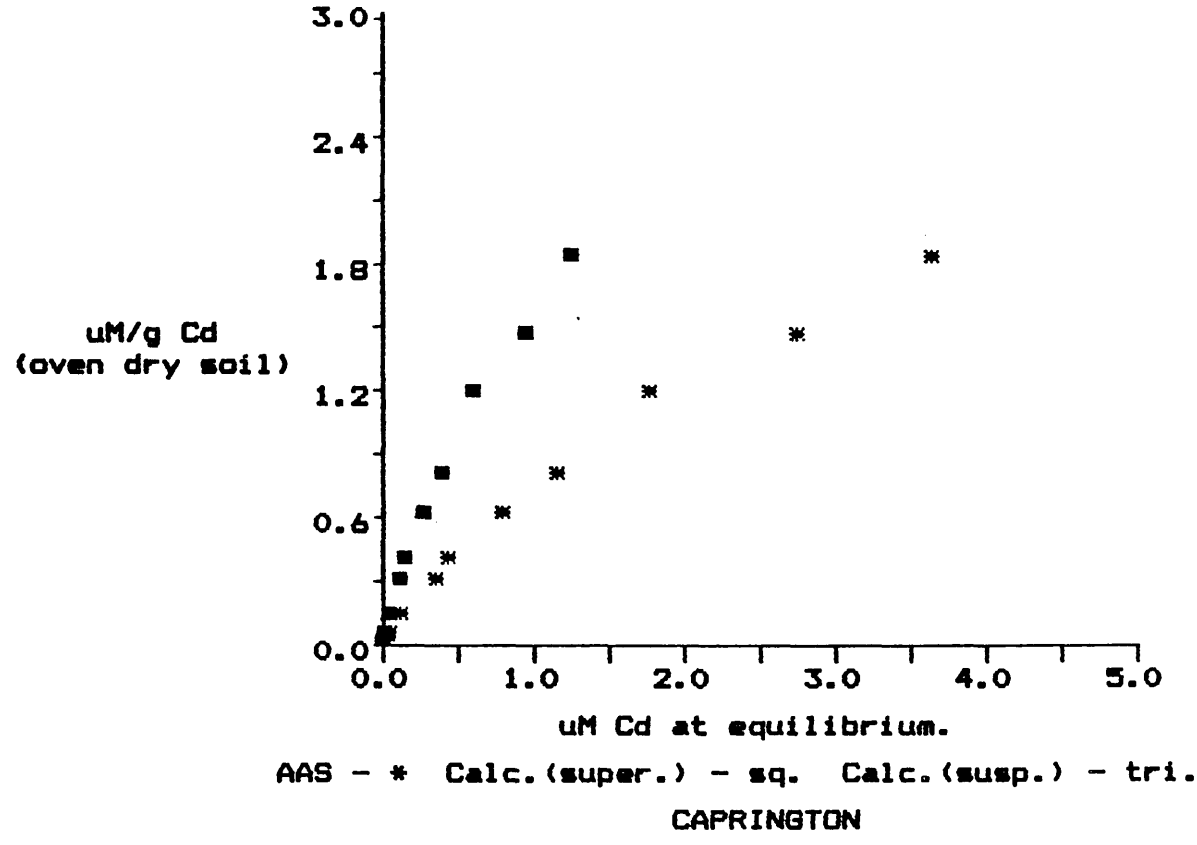
b



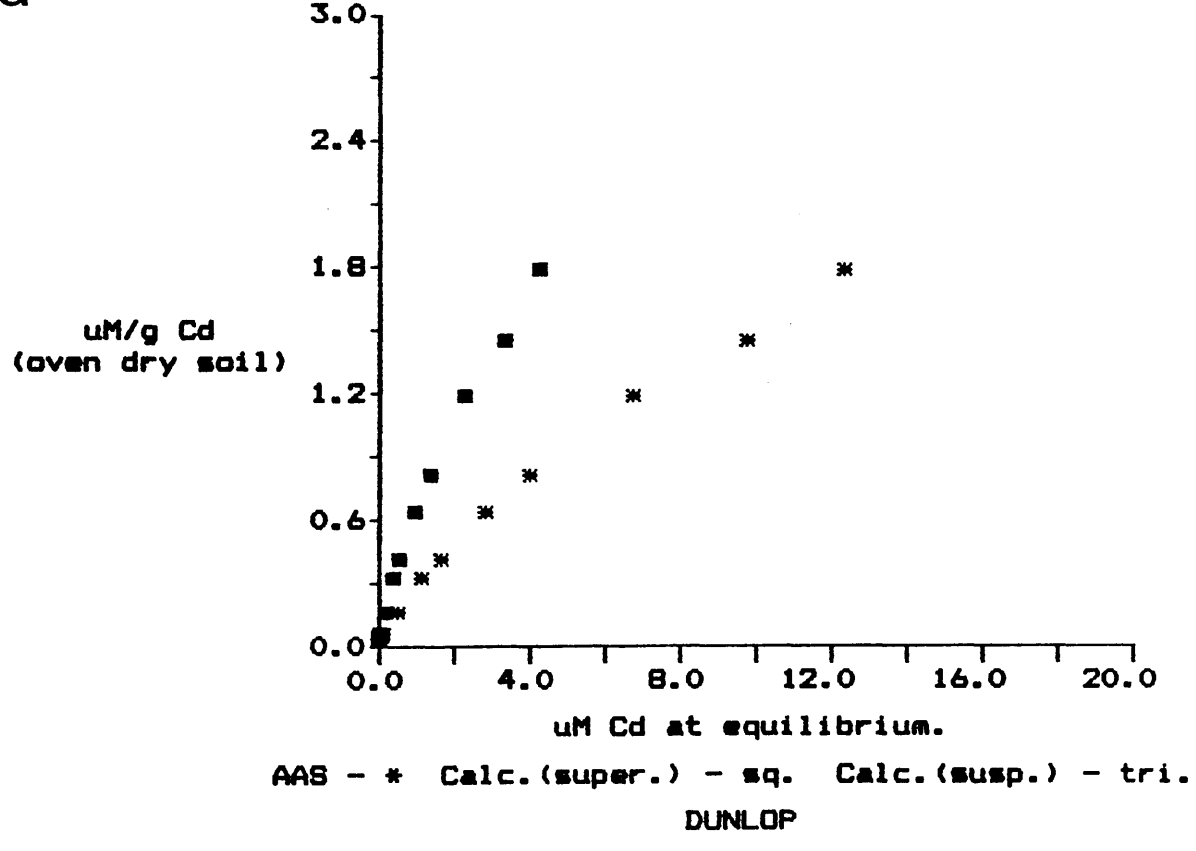
AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

ARKLESTON HIGH ZINC

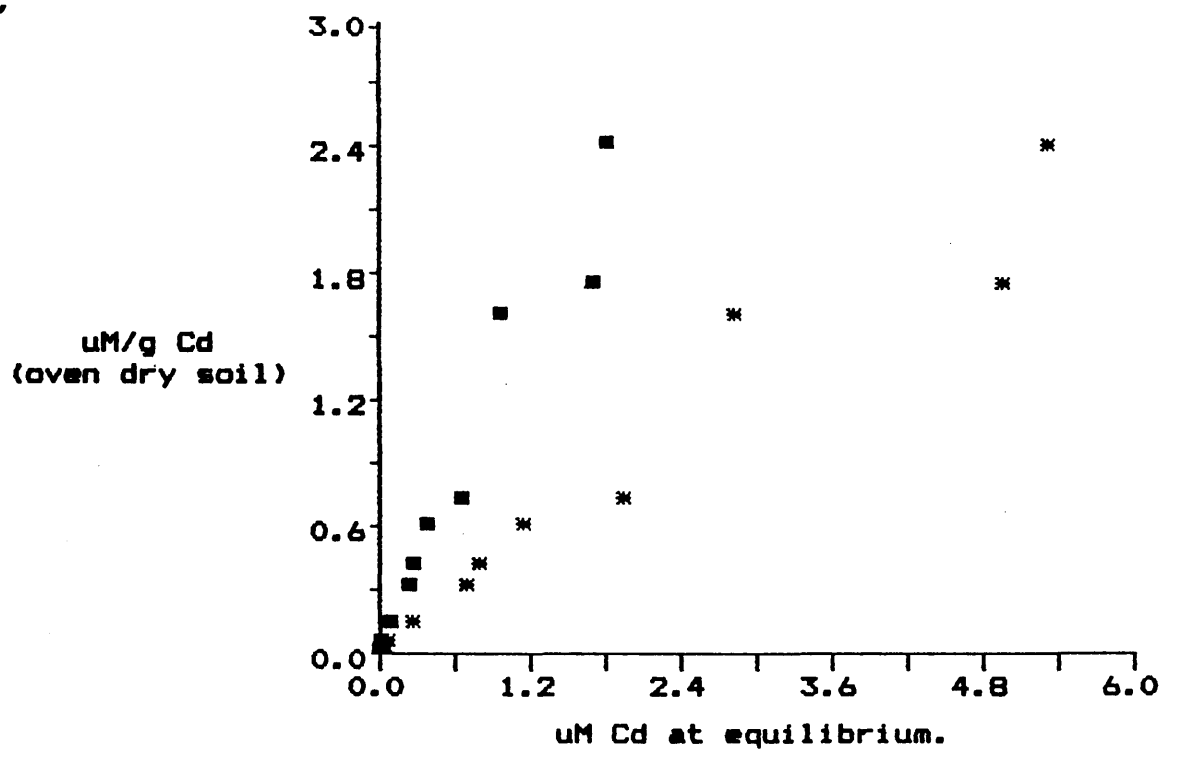
c


3.0
2.4
1.8
1.2
0.6
0.0
uM/g Cd
(oven dry soil)
0.0
1.0
2.0
3.0
4.0
5.0
uM Cd at equilibrium.
AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.
CAPRINGTON

d


3.0
2.4
1.8
1.2
0.6
0.0
uM/g Cd
(oven dry soil)
0.0
4.0
8.0
12.0
16.0
20.0
uM Cd at equilibrium.
AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.
DUNLOP

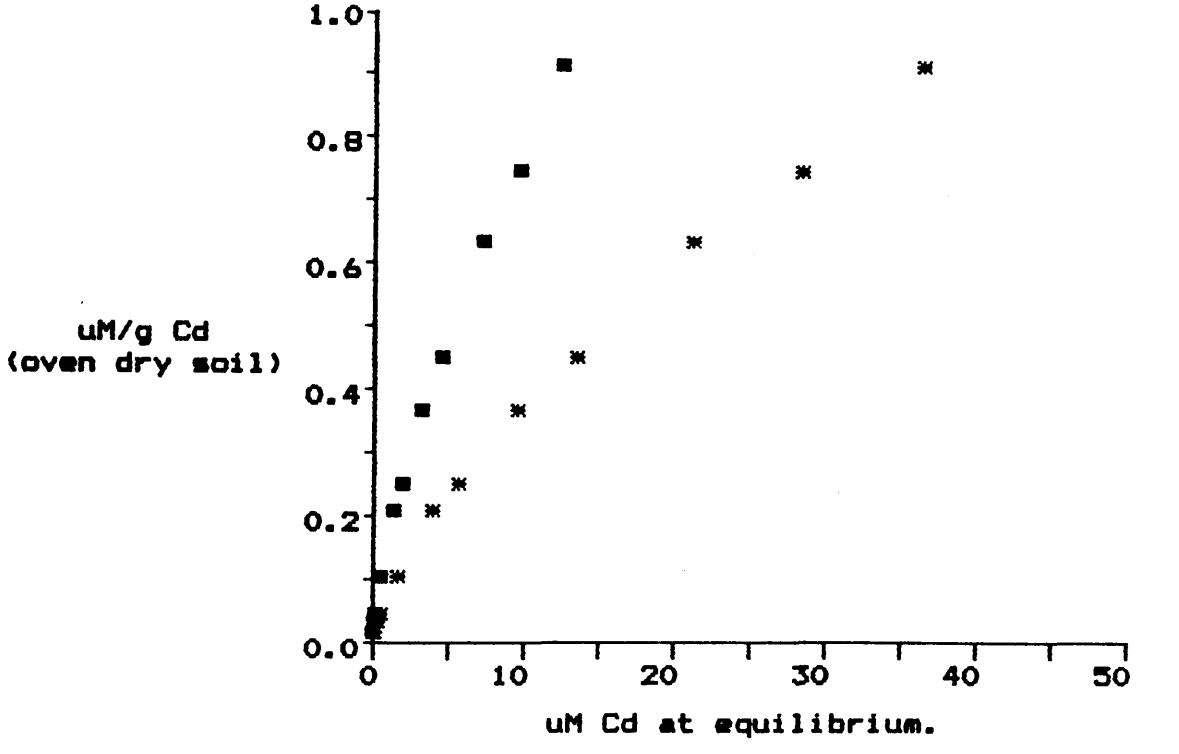
e



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

BLACKSTOUN ALLUVIAL

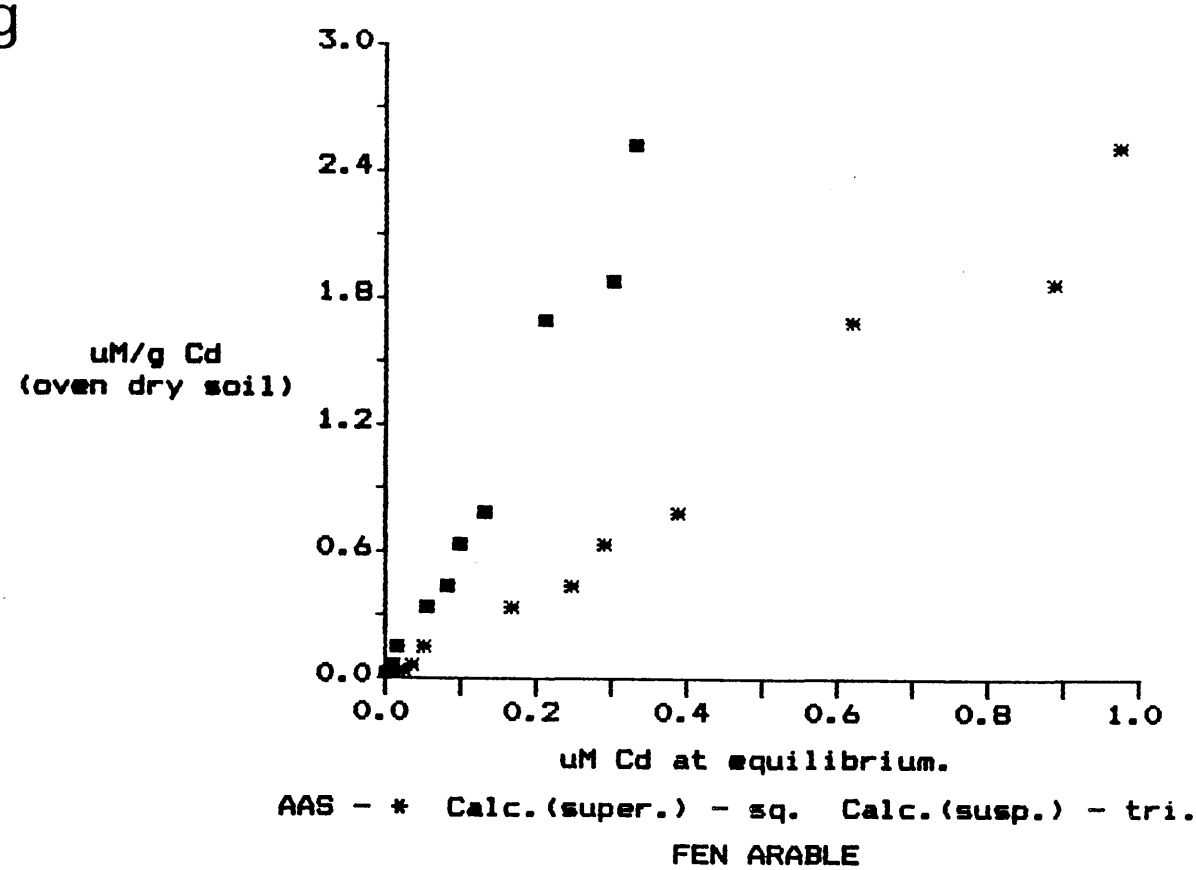
f



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

DREGHORN

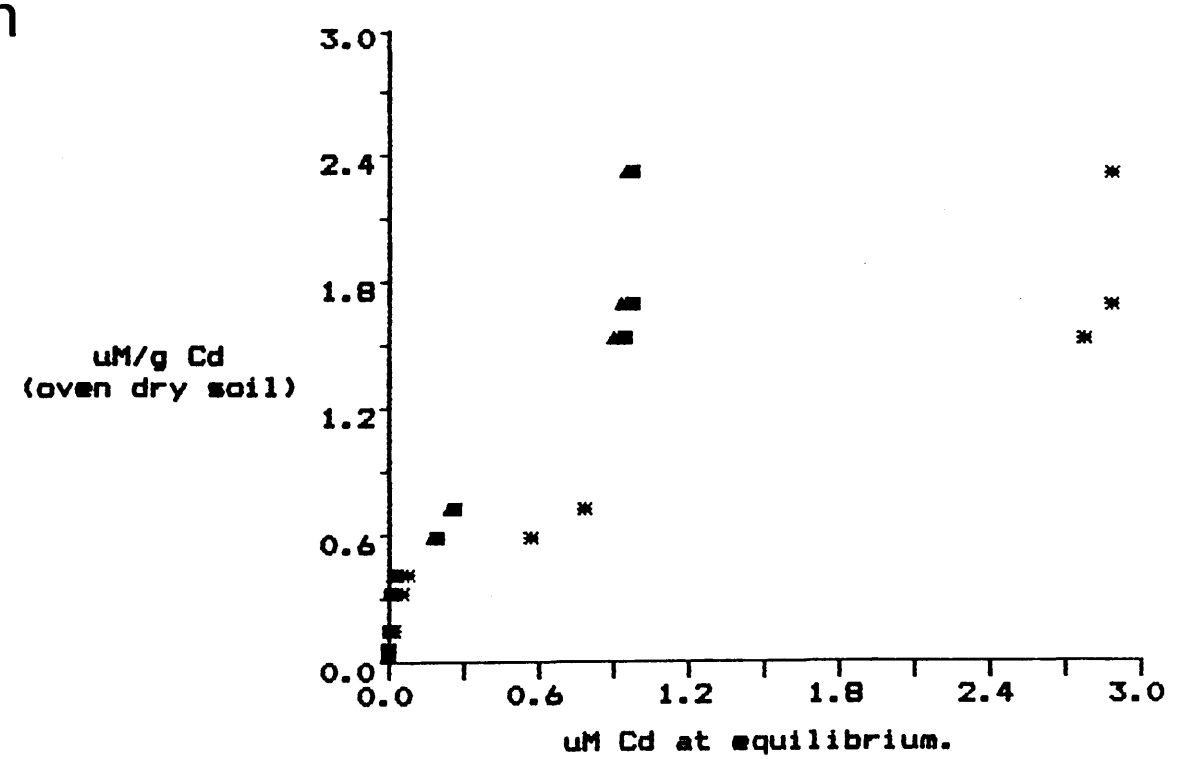
g



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

FEN ARABLE

h



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

FEN SUBSOIL

Figures 3.18. and 3.19. Cu and Cd AAS, ISE and Calculated Activity Freundlich Sorption Isotherms.

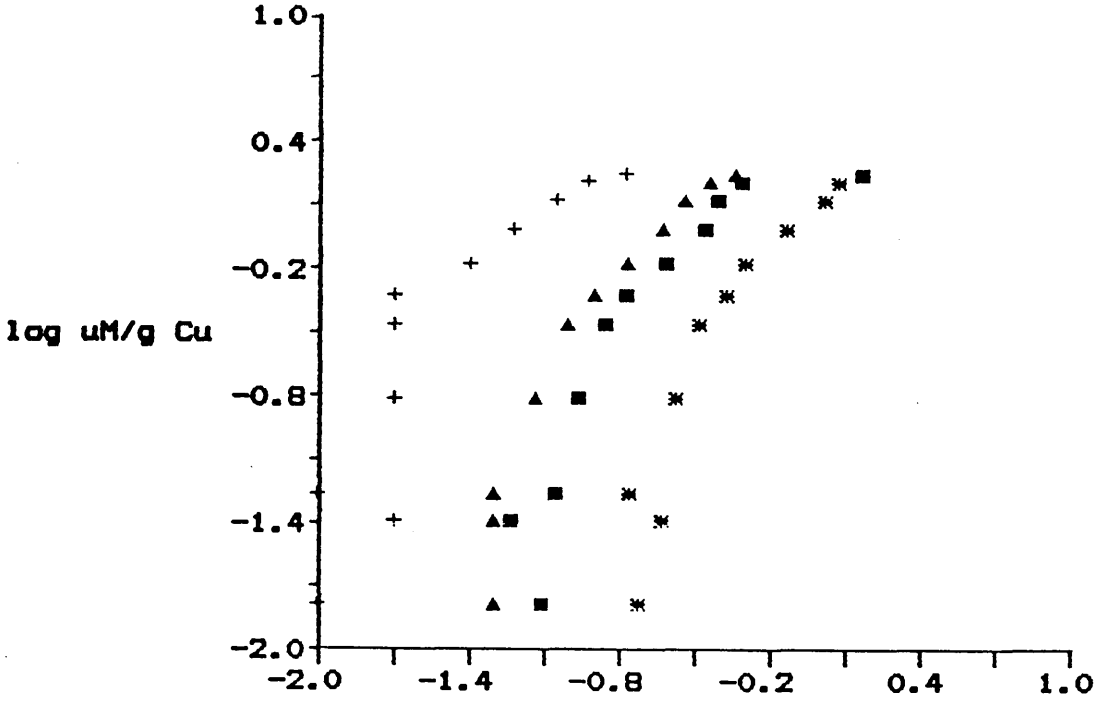
Figure 3.18. Cu AAS, ISE and Calculated Activity Freundlich Sorption Isotherms.

(a). Ark.
(b). AHZ.
(c). Cap.
(d). Dun.
(e). BA.
(f). Dreg.
(g). FA.
(h). FS.

Figure 3.19. Cd AAS, ISE and Calculated Activity Freundlich Sorption Isotherms.

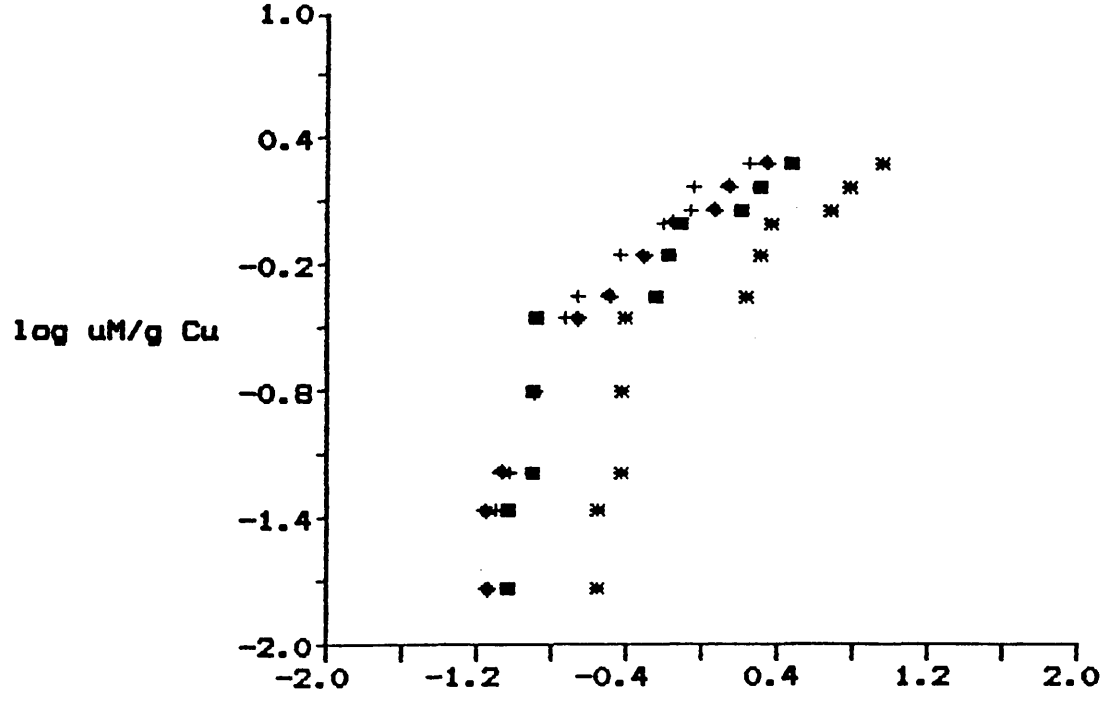
(a). Ark.
(b). AHZ.
(c). Cap.
(d). Dun.
(e). BA.
(f). Dreg.
(g). FA.
(h). FS.

a



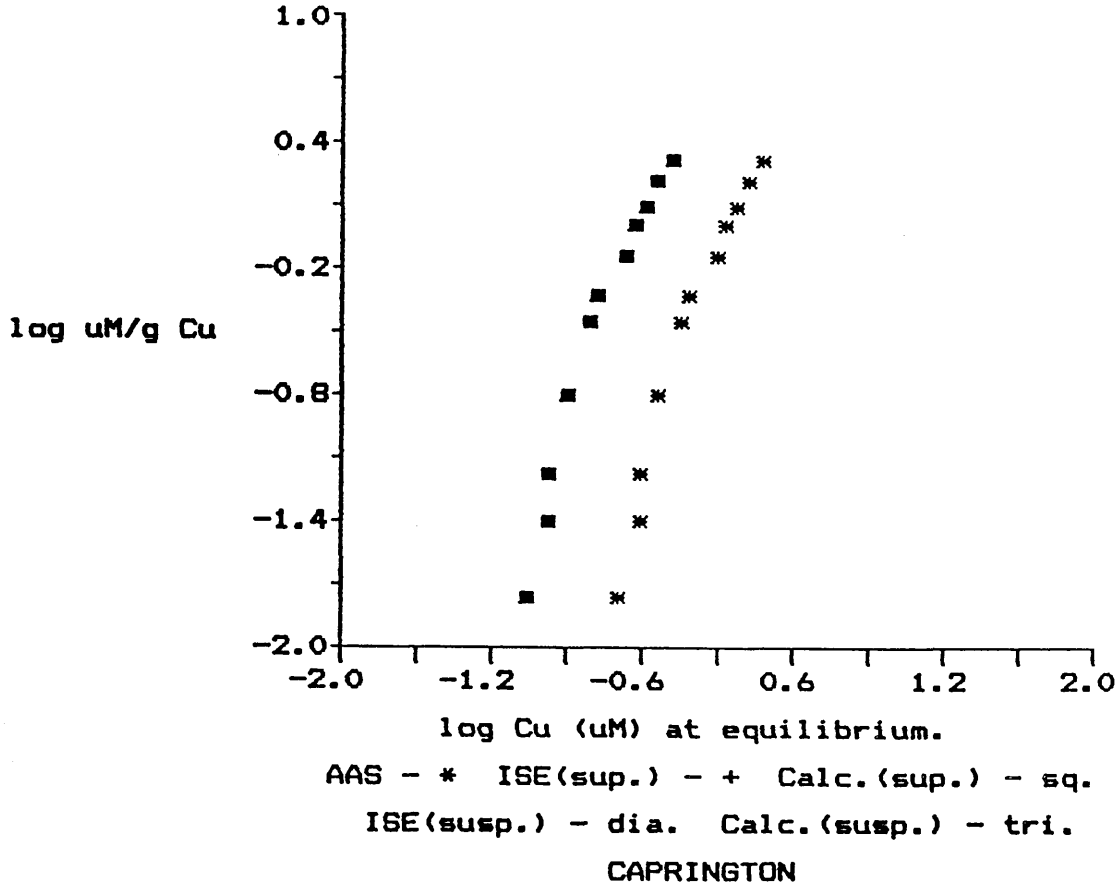
AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
ARKLESTON

b

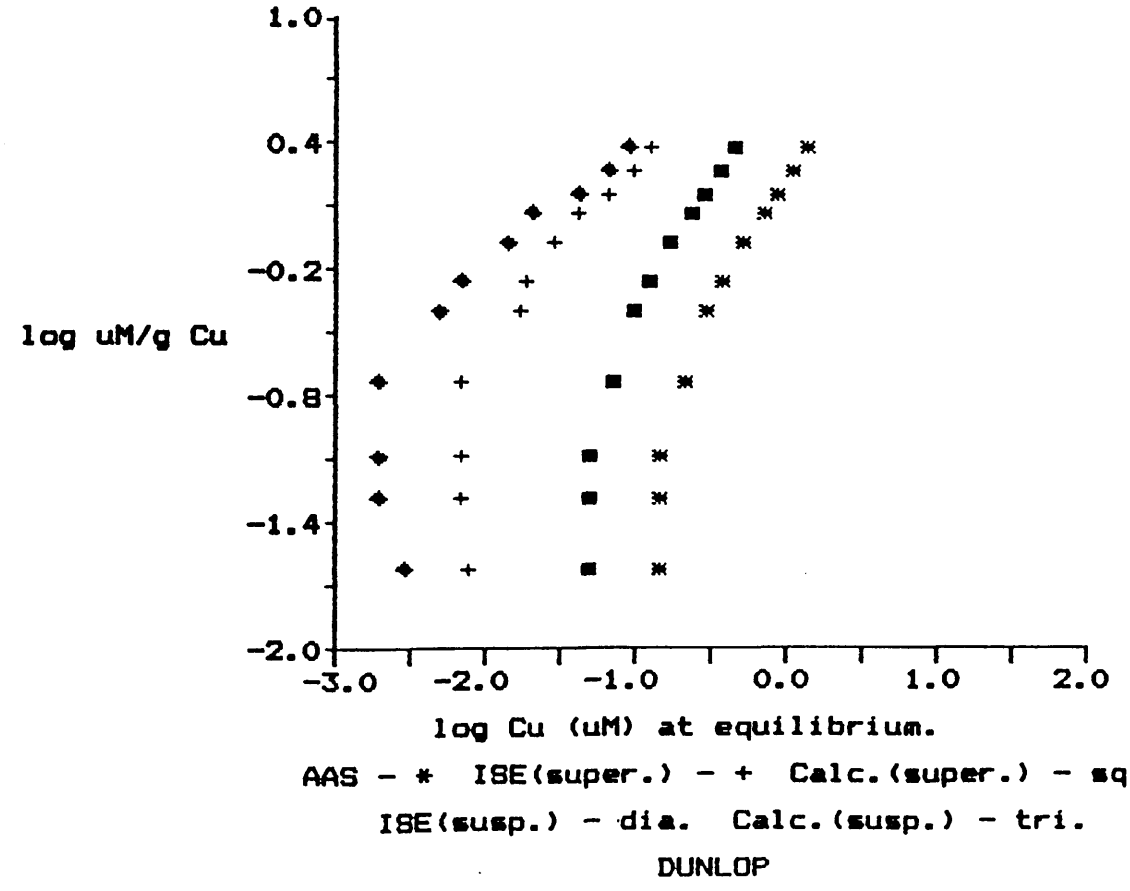


AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
ARKLESTON HIGH ZINC

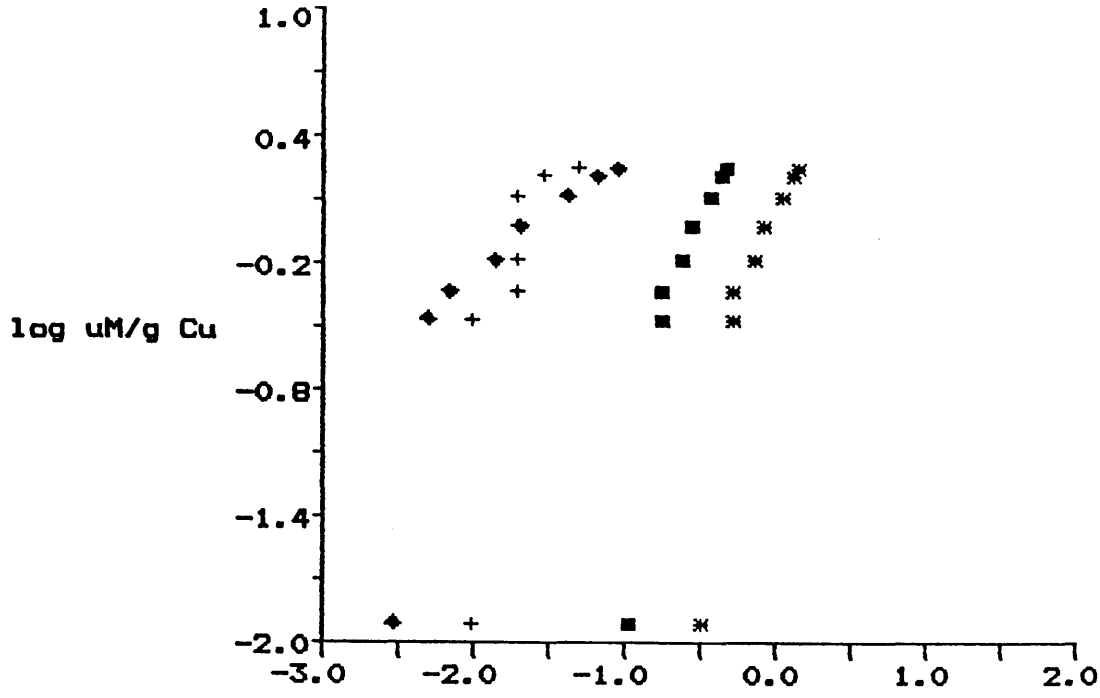
c


1.0
0.4
-0.2
-0.8
-1.4
-2.0
log uM/g Cu
-2.0
-1.2
-0.6
0.6
1.2
2.0
log Cu (uM) at equilibrium.
AAS - * ISE(sup.) - + Calc.(sup.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
CAPRINGTON

d

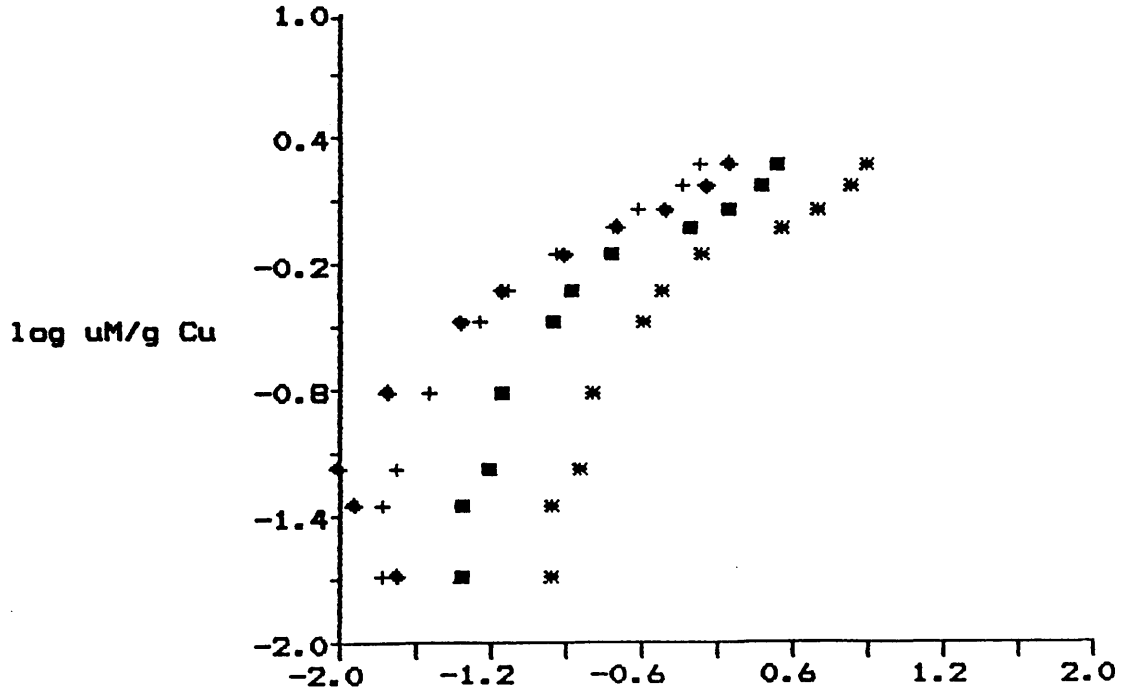

1.0
0.4
-0.2
-0.8
-1.4
-2.0
log uM/g Cu
-3.0
-2.0
-1.0
0.0
1.0
2.0
log Cu (uM) at equilibrium.
AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
DUNLOP

e



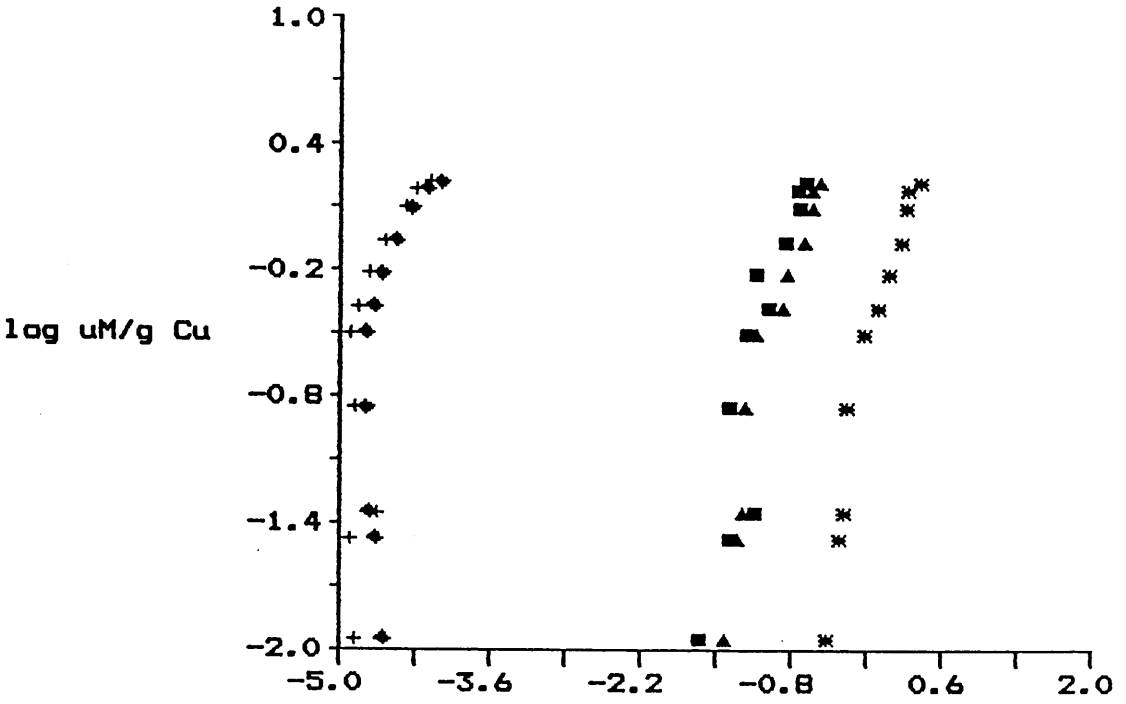
AAS - * ISE(sup.) - + Calc.(sup.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
BLACKSTOUN ALLUVIAL

f



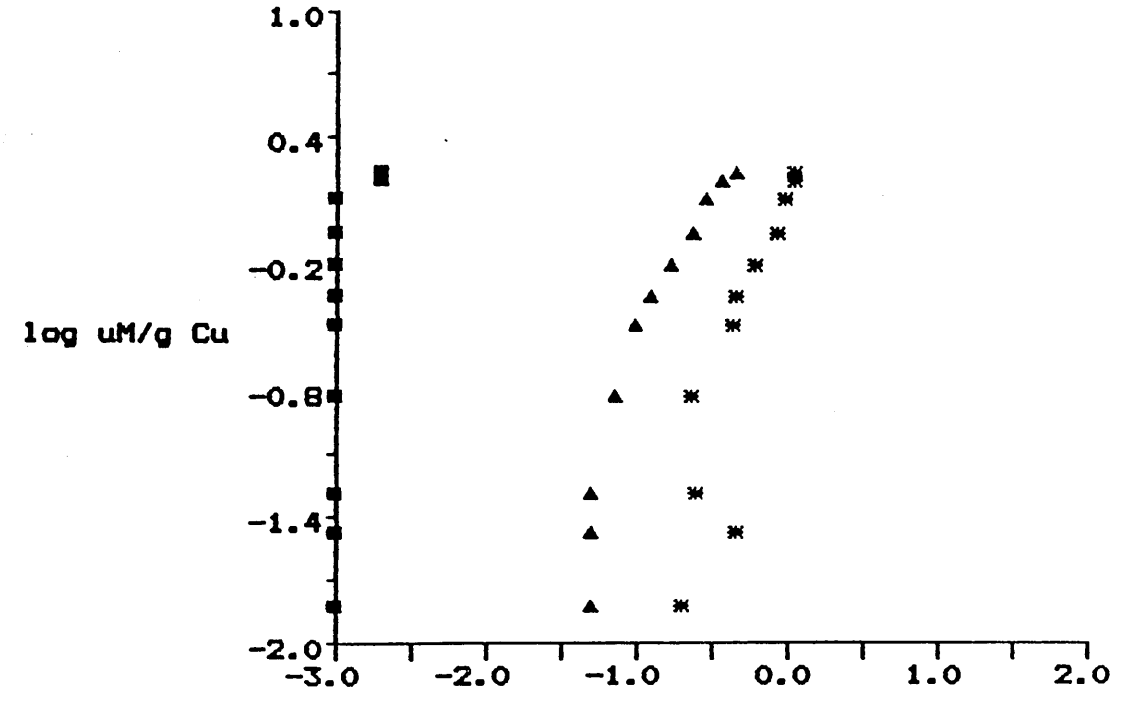
AAS - * ISE(sup.) - + Calc.(sup.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
DREGHORN

g



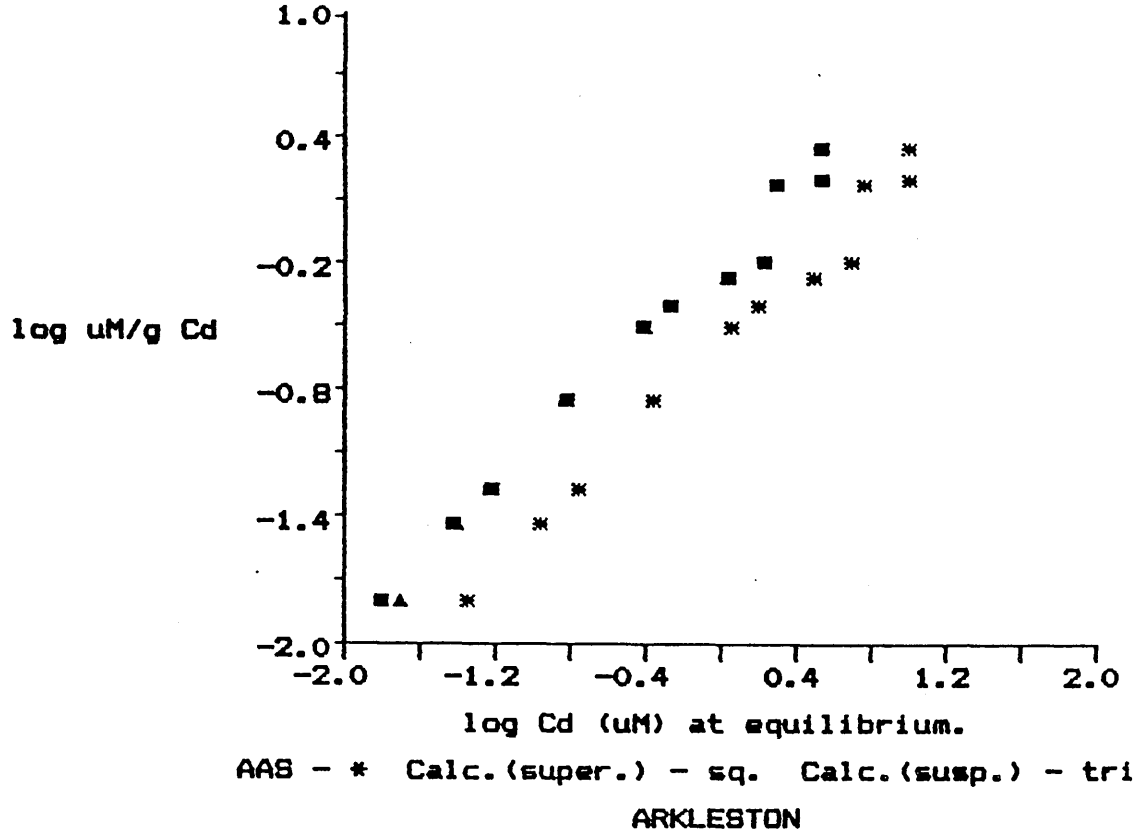
AAS - * ISE(sup.) - + Calc.(sup.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
FEN ARABLE

h



AAS - * ISE(super.) - + Calc.(super.) - sq.
ISE(susp.) - dia. Calc.(susp.) - tri.
FEN SUBSOIL

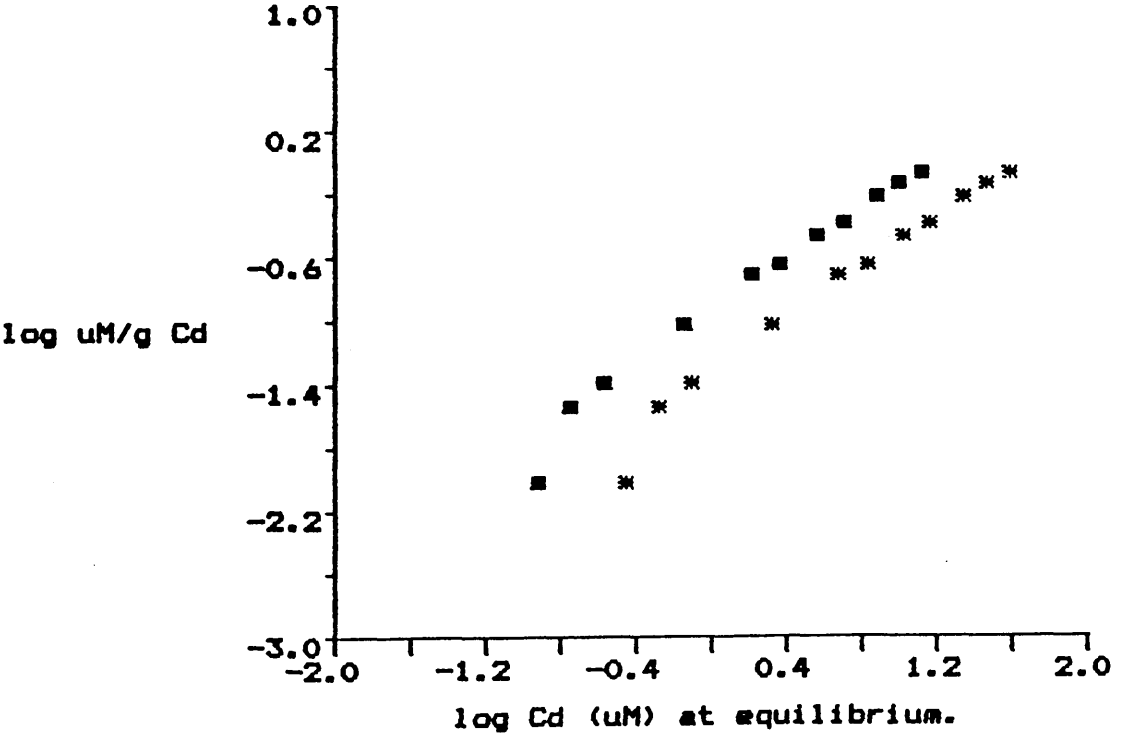
a



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

ARKLESTON

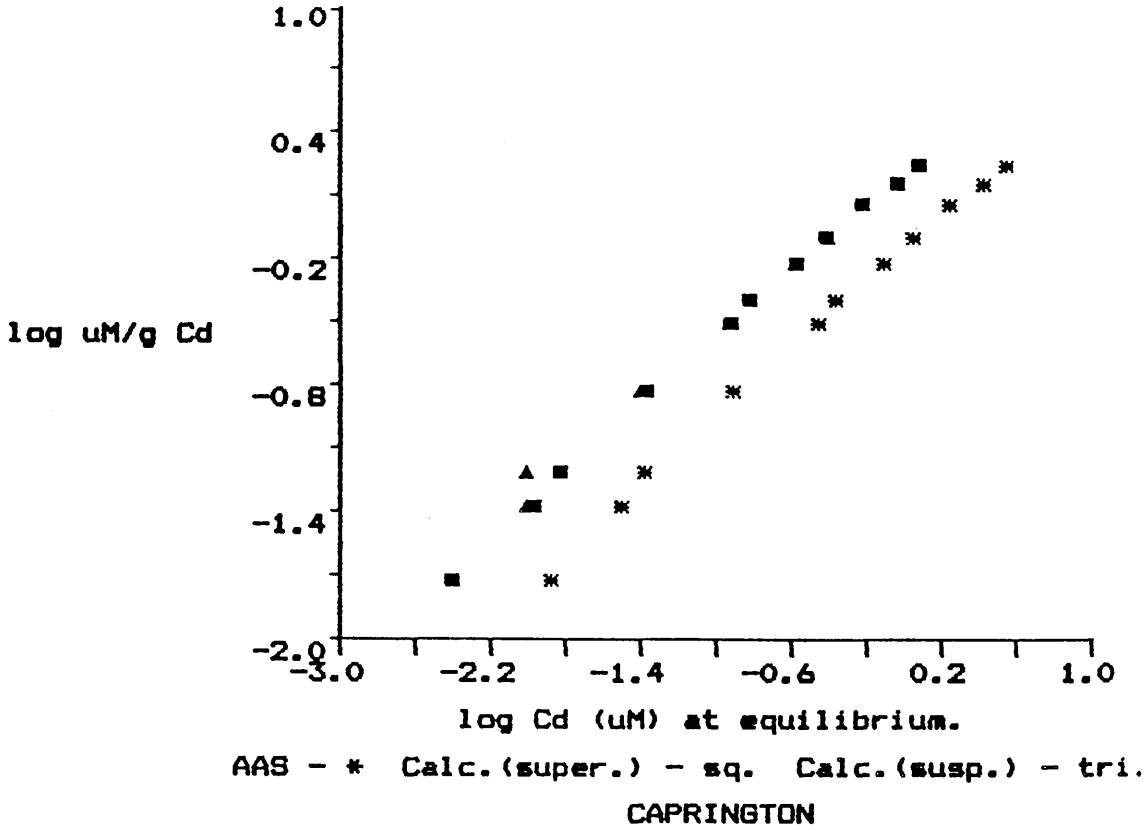
b



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

ARKLESTON HIGH ZINC

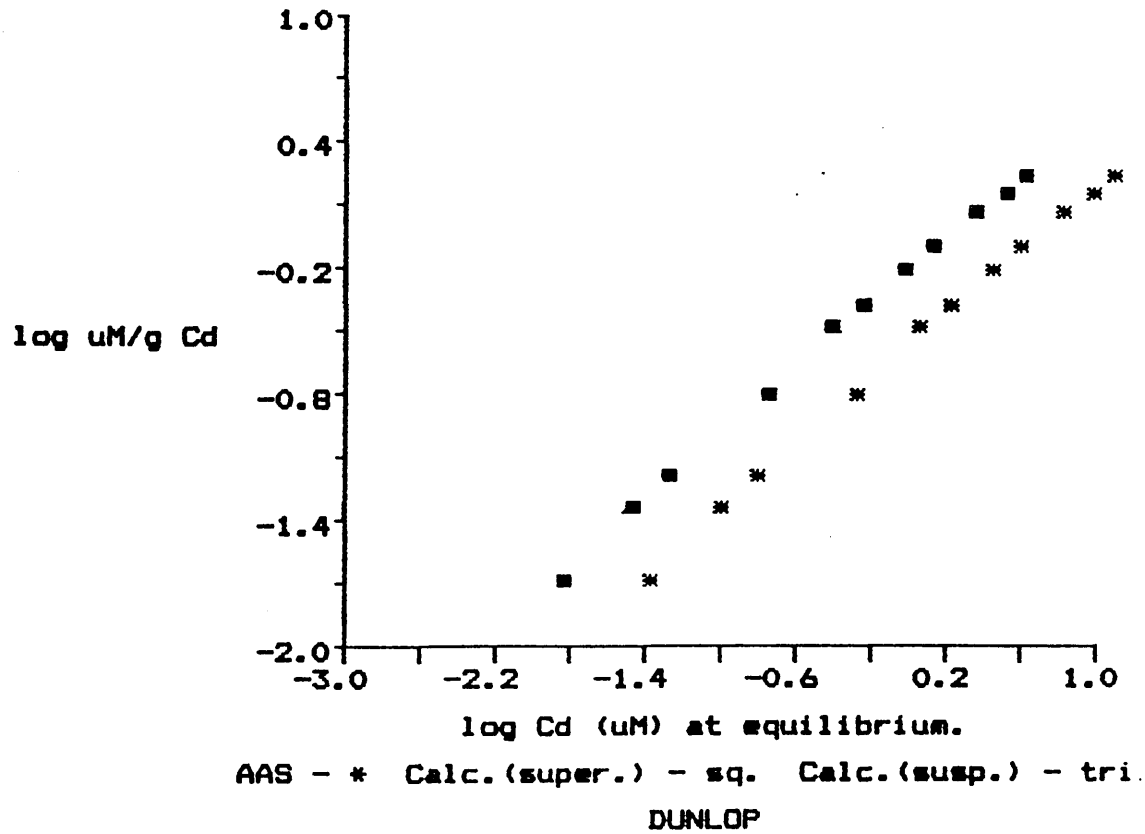
c



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

CAPRINGTON

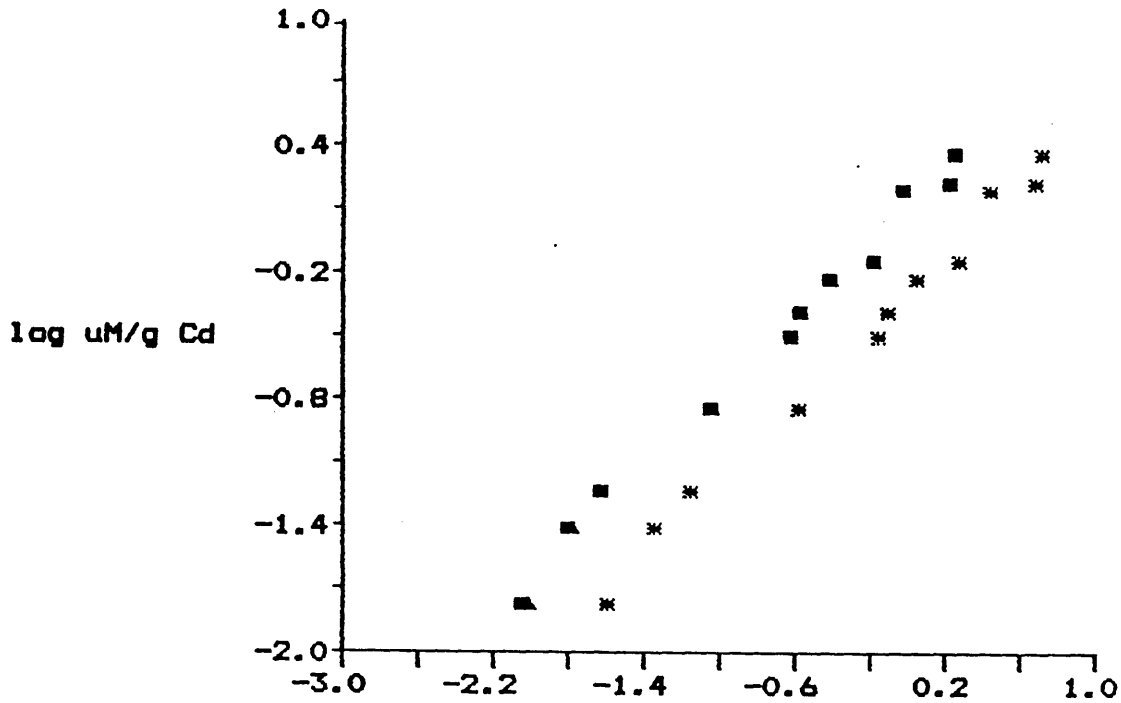
d



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

DUNLOP

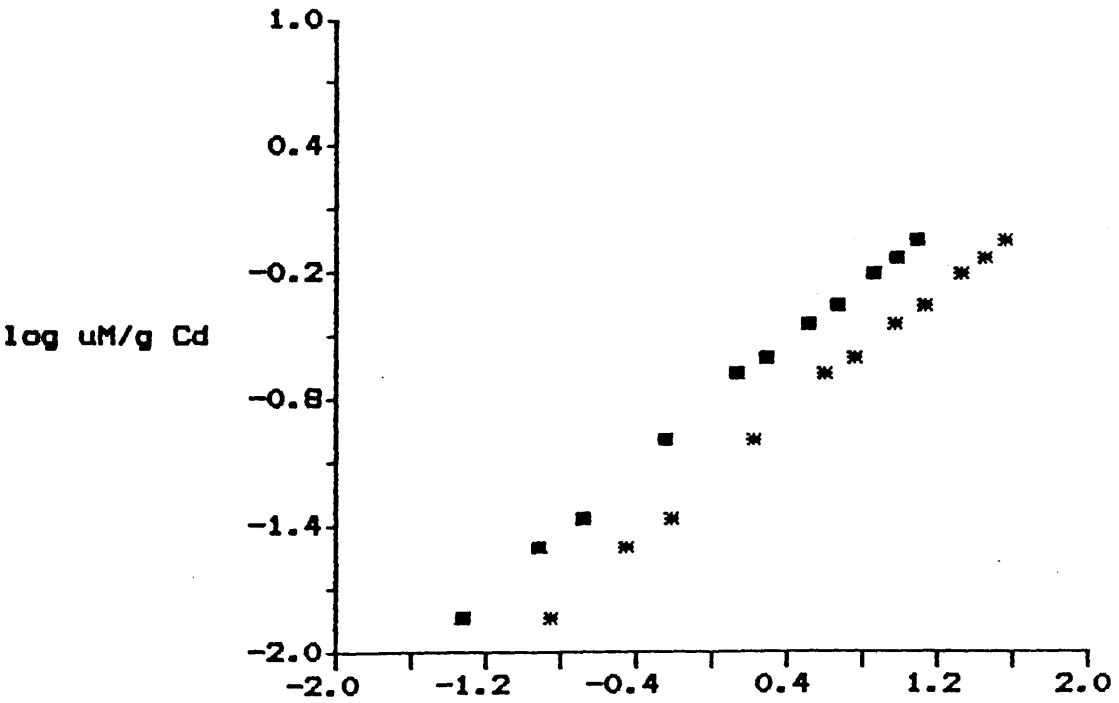
e



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

BLACKSTOUN ALLUVIAL

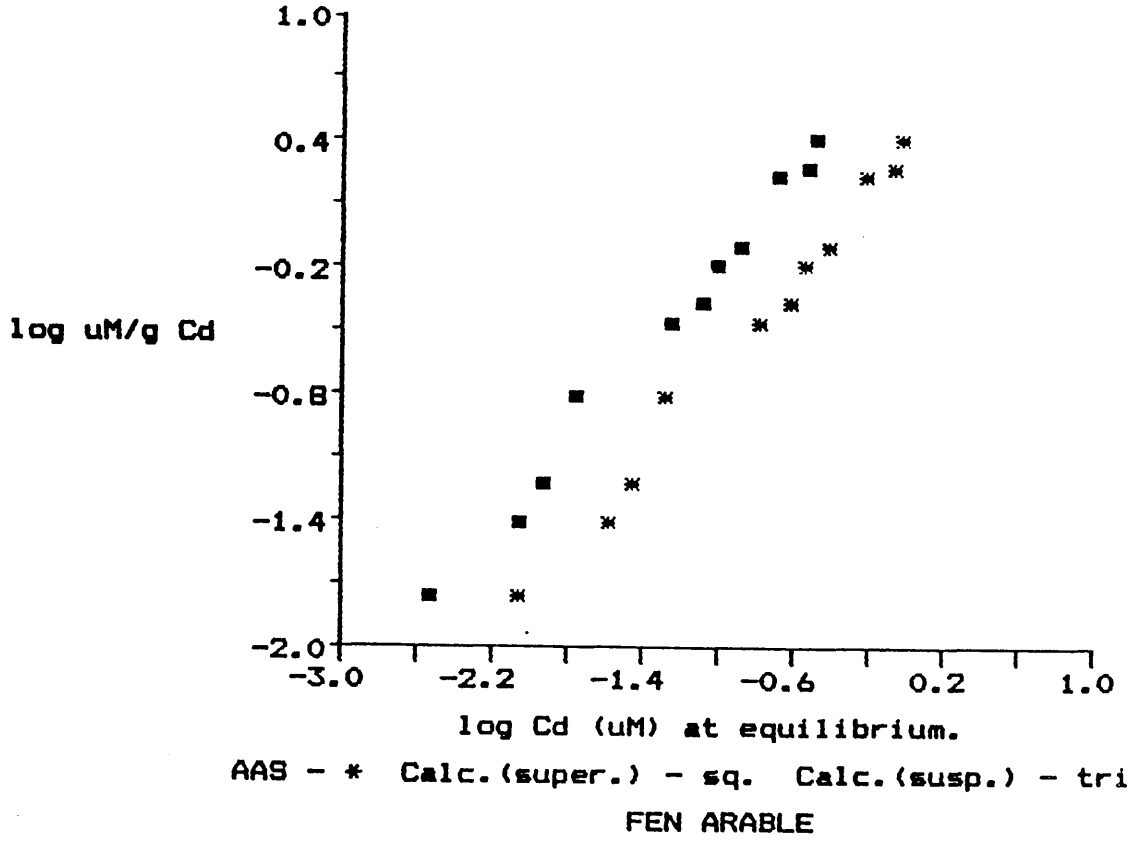
f



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

DREGHORN

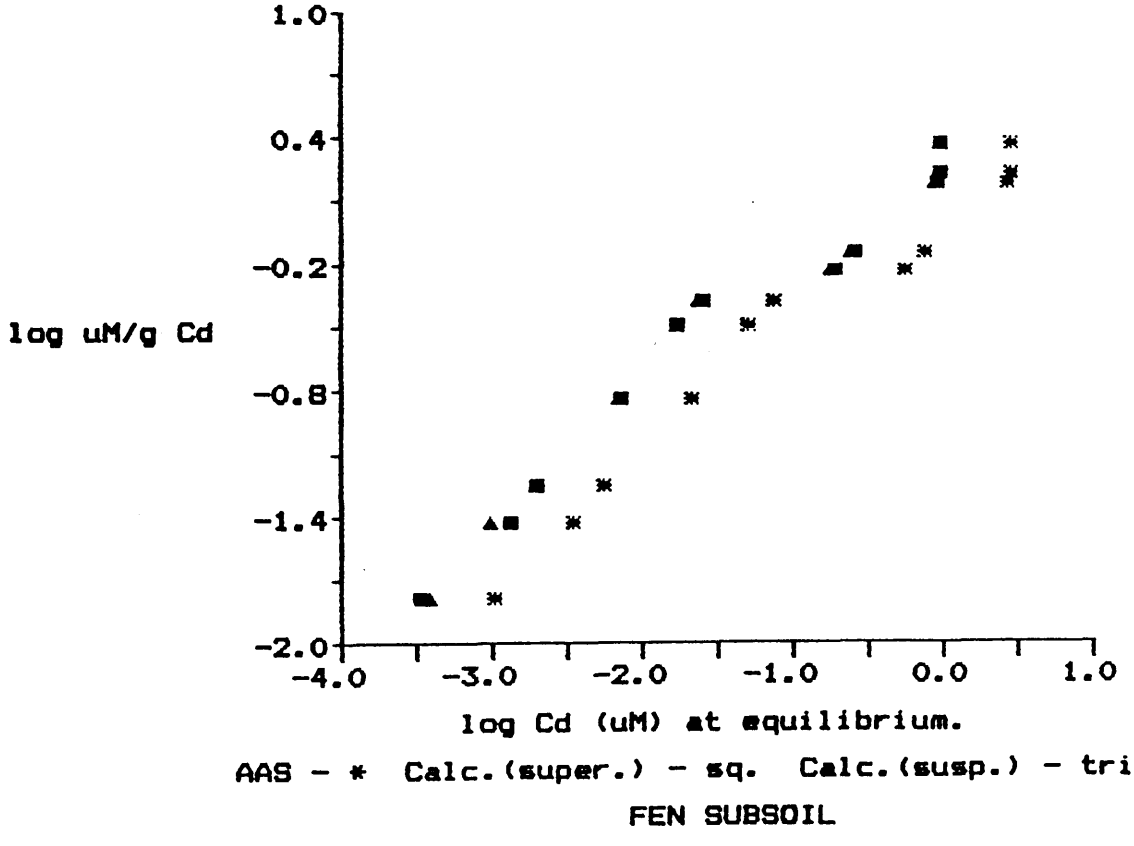
g



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri.

FEN ARABLE

h



AAS - * Calc.(super.) - sq. Calc.(susp.) - tri

FEN SUBSOIL

3.3.1.3. Discussion of Sorption Experiments.

When comparing the uptake of Cd and Cu on to most sorbent surfaces, Cu is always taken up to a greater degree than Cd, under the same conditions of I, pH and temperature (*cf.* table 1.9. and table 1.10.), with the possible exception of sorption on to Calcite. Turning to the literature comparisons of whole soils and the two elements, Dudley *et al* (1988) demonstrated this order of affinity, as have Cavallaro and McBride (1978), Doner (1978), and Petruzzelli *et al* (1985). The study by Dudley is particularly interesting, as the sorption is measured on Calcareous soils (pH 7.9 and 8.6), and runs contrary to what has been found in this study, ie. that high native levels of Calcite will favour Cd retention over Cu: only the work of Kuo and Baker (1980) shows enhanced retention of Cd over Cu (on acid soils).

Background Electrolyte and Protons and the Sorption Reaction.

Non-specific interactions have been largely ruled out in this series of experiments, by the use of 0.1M $NaNO_3$ as the background matrix: consider -

CEC = 18me/100g = 306μe of charge per sample used in the equilibration.

50mls of 0.1M $NaNO_3$ = 5000μe of charge.

e = equivalent

ie. Na^+ is present at 17x the total number of available CEC sites.

It may be assumed that the reactions being observed are very specific ones. This statement gains further credence in view of the lack of evidence of Cd or Cu exchange with Fe, Mn or Ca, and, most importantly, protons. These facts largely rule out the consideration of well-known

precipitation reactions (as in section 3.1.1.) and of exchange reactions at the surface of Fe/Mn oxides or at Calcite. As pointed out in that section, the presence of non-protonated Lewis bases cannot be eliminated, and these sites, such as those on organic colloids, may be the destination of the Cu and Cd ions. In agreement with Sposito's views on the subject (Sposito, 1984), the word 'adsorption' cannot be applied to the process being observed, as yet, but the peripheral evidence is quite strong.

The absence of any gross change in the pH of the systems, except at very high loadings of metal, effectively negates the idea of changes in the slope of the curves being due to alterations in the speciation of the systems (this would be true even if the organic interactions could be quantified); the only other speciation option concerns the formation of poly-nuclear species, which is unlikely unless solution levels which result in precipitation are approached. To alter the pH of a solution at pH 5.5, to 5.4 requires the addition of, in 50mls.;

$(H_i^+) = 3.16 \times 10^{-6}$ moles of protons.(pH 5.5).

$(H_f^+) = 3.98 \times 10^{-6}$ moles of protons (pH 5.4).

$\Delta(H^+) = 4.10 \times 10^{-8}$ moles of protons.

The same argument holds for a soil suspension: 1.7g of oven dry soil in 50mls in these experiments would have to release 4.10×10^{-8} moles of protons to bring about such a pH change. Given that two typical values for Cd and Cu uptake could be;

Cd: 1.76 μM/g = 148x

moles of protons released above.

Cu: 2.26 μM/g = 187 x

(if the change is 4.5_>4.4, these factors are lower by ≈ a

factor of ten, similarly if the change were 6.5->6.4, they would be greater by a factor of ten).

Thus, pH changes at a higher order of detection (3rd decimal place) may have to be observed if the changes which are due to uptake of metals are to be noted, but this leads to imprecision and uncertainty in measurement, as at this order of magnification it will take the system, because of its heterogeneous nature, a very long time to achieve any position which could reasonably be judged to be at equilibrium. This said, the fact that Cd and Cu are being taken up to levels which suggest that if they were displacing protons much greater changes in pH would be being observed, and they are not, suggests that protonated sites are not the ones which specifically take up Cd and Cu (many of these H^+ bearing sites may, anyway, have succumbed to the mass action 'pressure' of Na^+).

Correlation of Soil Properties and Sorption Parameters.

Attempts have been made to correlate the properties of soil uptake (isotherm gradients, Freundlich gradients, intercepts and Langmuir constants) with the basic soil properties (pH etc.), but no significant relationship could be found for either Cd or Cu. This concurs with the findings of Brown *et al* (1983) and McLaren *et al* (1983) for Cu. Jarvis (1981) states a similar lack of correlation between the basic soil properties and the uptake parameters of Cu, although he did find a slight inter-relationship between Cu uptake and pH.

Isotherm Shapes.

Looking now at the shapes of the isotherms found in this study, table 3.9. is presented as a summary of the findings of other authors, as a basis for comparison:

Table 3.9. Isotherm shapes.

Cd

Shape	Reference
S - removal of OM results in L.	Neal and Sposito (1986)
L	Levi-Minzi *et al* (1976)
L	Christensen (1984)
L and H	Narvot *et al* (1978)
L	Cavallaro and M^{c}Bride (1978)
C	Jarvis and Jones (1980)
C	Garcia-Miragaya and Page (1978)
C	Petruzzelli *et al* (1985)

Cu

Shape	Reference
H and L	Cavallaro and M^{c}Bride (1978)
H and L	van Bladel *et al* (1988)
L	M^{c}Laren and Crawford (1973b)
C	M^{c}Laren *et al* (1983)
C	Jarvis (1981)
C	M^{c}Laren *et al* (1981)

L and H shapes predominate the findings of others, and, certainly for Cd, the results presented in this chapter confirm this viewpoint, although, at the low concentrations the constant partition description has been shown to describe Cd uptake (Garcia-Miragaya and Page (1978), Jarvis and Jones (1980)). The line between C and H description is very much determined on a comparative scale; plotted on expanded axes, the lower end of an H isotherm could be construed as being of C character, so perhaps the results are not so different. Given the range of soils studied here and in the table above, Cd shows a remarkable degree of consistency in its behaviour, as categorised by this approach.

At relatively high levels, the Cu isotherms agreed with the literature reports and display H and L shapes. Examining

the lower end of the Cu isotherms again brought agreement with the findings presented elsewhere, in displaying C behaviour. An aspect of behaviour of metals which has been shown for Cd by Neal and Sposito (1986) and a similar relationship for Cu in the work of McBride and Blasiak (1979), is the S type isotherm, in this chapter demonstrated for 4 soils in relationship to Cu. Neal and Sposito (1986) clearly showed that this shape could be ascribed to the soluble organic matter, and certainly the results presented here (and in table 2.1.) would concur with this. More evidence for this role is presented by the ISE figures, which gave rise to the H isotherms in the soils, which in concentration terms,gave S isotherms. The High Zinc and Dreghorn soils, which have the lowest organic matter content and the lowest pH's maintain their H character, even when the ISE figures are used, which indicates the insignificance of soluble organic matter in the solution chemistry of these soils.

Conferring with the summary tables of previous studies found in the literature (1.11. and 1.12.), the van Bemmelen-Freundlich description is the best equation for the description of the Cd data, which is borne out by the findings of this work , over several orders of magnitude of concentration. There seems to be little connection, though, between the shape, as defined by Giles *et al* (1974 a and b), of the C v X isotherm and the best fitting mathematical description of the data. The results of this work produced L or H isotherms, which were best described by a log-log relationship. Others have found that a C isotherm fits this relationship (Garcia-Miragaya and Page, (1978)) and may be described by a two constant version of this equation (Jarvis and Jones, (1980)). In only one study, that of Narvot *et al*

(1978), could the sorption process be described by a two constant Langmuir, whereas most of the sets of data in this study could be reproduced by fitting them to this type of equation.

A greater variety of equations has been used to describe the reaction of copper with soils, which is in agreement with the difficulty encountered here in finding any simple mathematical relationship which will perform as well as the van Bemmelen-Freundlich does for Cd, over such a wide range of concentrations. In table 1.12., the suitability of the Langmuir isotherm to the task outweighs the number of applications of the log-log relationship, and it is impossible to ascribe this difference in the ranges of applicability to the areas of concentration studied. In contrast to the situation found with Cd, the approach for Cu would appear to be very much one of 'horses for courses'. However, the range of concentrations which can be covered with the logarithmic equation favours its use, even with the curvature experienced here with Cu data. The splitting of this relationship into two sections coincides with the findings of Jarvis (1981) and Ritchie and Jarvis (1986), although this is not, in my results, found to occur solely with the two highly Calcareous soils. The presence of hydrolysis products is likely to be insignificant at pH values < 6, but, as pointed out by Ritchie and Jarvis (1986), at >100μM Cu the influence of bi-nuclear complexes may begin to be seen, and at the higher end of the isotherm this may explain the reduction in the gradient (as seen in the van Bemmelen-Freundlich plots). Ritchie and Jarvis (1986) attempt to explain the phenomenon purely in terms of the inorganic speciation. Given that organic stability constants from logK = 4.1 (Mench *et al*, (1988)) to logK = 7.3

(Stevenson, (1977)) can be found in the literature, and that these complexes compete ably with surfaces for Cu (McBride (1981)), it is not unreasonable to suppose that if the soluble organics are at saturation, the inorganic speciation can describe the more labile, active part of the solution.

It must be borne in mind that using the logarithmic plot in these experiments, it is being applied in terms of a necessity to summarize data over a wide range of concentrations. As pointed out by Sposito (1980, 1981), for the rigorous application of the van Bemmelen-Freundlich isotherm, the ß term (the gradient) has to fall between 1 and 0. Clearly this does apply with description of Cd, however, in only two instances (the soils with the lowest affinity for Cu - AHZ and Dreghorn) does this condition become satisfied with respect to Cu. Table 3.10. demonstrates some typical ß values found in the literature;

Table 3.10. Literature Values of the ß Term of the van-Bemmelen Freundlich Equation.

Element	Sorbent Material	ß	Reference
Cd	Amorphous Fe oxide	0.66*	Benjamin (1981).
Cu	" " " "	0.66*	*ibid.*
Cd	Na-Montmorillonite	0.767	Inskeep and Baham (1983).
Cu	" " " "	0.565	*ibid.*
Cu	Range of soils	5-24	Ritchie and Jarvis (1986).
Cu	Illite	0.804	McLaren *et al* (1981).
Cu	MnO_2	1.405	*ibid.*
Cu	Fe-oxide	1.032	*ibid.*
Cu	Peat	1.019	*ibid.*
Cd	Calcareous soils	0.95-1.30	O'Connor *et al* (1984).
Cd	Range of soils	≈5	Jarvis and Jones (1980).

* at low sorption density, ß⇒ 1.0.

This is of small concern here, as there is no attempt to read anything regarding the nature of the reaction into the fact that the data can be described by a given equation; quite simply, from the van Bemmelen-Freundlich gradients we may say that the affinity of soils for inputs of Cu is very great, and this specificity continues at quite high concentrations.

The chemical reactions controlling the levels of cations and anions in solution are complex. It has been proposed by several authors (Lindsay (1979); Brummer *et al* (1983); Pulford (1986)) that solubility considerations may be responsible for dictating the levels of certain elements. Most of the well known and characterized solid phases have equilibrium constants which permit far higher levels of metals than are found in soil solutions - this may just reflect the degree of heterogeneity of the soil minerals, or the amorphous nature of such materials. Hypothetical compounds such as 'Soil-Cu' and 'Soil-Cd' have been proposed by Lindsay (1979) to account for this problem. Lindsay, in the same book, also proposes a Cu-Ferrite compound to explain Cu solubility phenomena, whilst, drawing on the well documented affinity of Cd for $CaCO_3$ has led Gorbatov (1988) to suggest the formation of $CdCO_3$ in high pH Calcitic soils. If we are observing a precipitation reaction or simply an exchange phenomenon, then it is likely that changes in pH or other cation levels would be detectable. With the first set of isotherms, only above $\approx$350μM initial metal concentration did changes in pH become noticeable. Solid-solution theory (see Stumm and Morgan (1981), p.285) allows for low concentration precipitation of trace substances (ie. below saturation with respect to a given well characterized solid phase),

effectively by a reduction in the solubility product of the material, but , at 350μM, the concept of 'trace' elements is not really applicable. The presence of a constant relationship between pH and pM^{n+} may indicate the existence of a precipitation; some sample figures are given in the following table (3.11.).

Table 3.11. pH v log metal concentration.

Soil-Element	Equation	r^2
Ark-Cu	$\log Cu^{2+} = 9.97 - 1.61pH$	0.964
AHZ-Cu	$\log Cu^{2+} = 13.18 - 2.40pH$	1.000
Cap-Cu	$\log Cu^{2+} = 14.75 - 2.50pH$	0.887
Dreg-Cu	$\log Cu^{2+} = 16.83 - 3.29pH$	0.992
Cap-Cd	$\log Cd^{2+} = 23.70 - 3.99pH$	0.967
FA-Cd	$\log Cd^{2+} = 29.14 - 4.09pH$	0.968
FS-Cd	$\log Cd^{2+} = 15.36 - 1.99pH$	0.998

Gorbatov and Zyrin (1988) found a relationship between the point of inflexion on a Kurbatov plot (pH v log Concentration) and a marked change in gradient of the sorption isotherm: this they attribute to highly specific sorption. No such clear cut relationship was found here, the sorption isotherms tending to progress to smooth curves at high sorption levels. The values for proton release, as quantified by the pH measurements, are similar to those found in the literature (see table 3.12. below).

Table 3.12. Litrature H^+ v M^{n+} Values.

Element	Sorbent	H^+ released	Reference.
Cu	a-FeOOH	1.8-2.4	Forbes *et al* (1976).
Cd	a-FeOOH	2.2	*ibid.*
Cd	'MnOOH'	1.3	Gadde and Latinen (1974).
Cd	Ca-Chernozem	2.3	Gorbatov and Zyrin (1988).

Only in one instance do my figures come very near to the idealized equivalent exchange of 2 protons for one M^{2+} (Fen Subsoil). The presence of gradients in excess of 2 suggests that it is not just being Cd or Cu involved in a sorption reaction, and may be interpreted as evidence for co-precipitation or co-sorption.

With the second set of isotherms there was no trend in pH changes, and the absence of any regular fluctuation in the concentration of major cations (Fe, Mn and Ca) discounts any possibility of the system being under the control of regular stoichiometric considerations, although without measurements of all possible displaced ions, this cannot be stated categorically. Certainly, at <350µM initial metal concentration, a highly specific sorption reaction is proceeding which may be adsorption.

Some Further Influences on and Influences of Speciation.

If we begin with a non-linear AAS isotherm, the production of a linear one from the ISE measurements, essentially a C-type isotherm would clearly be of great interest, indicating that the number of sites available for $(Cu^{2+})_{free}$ is far below the degree of saturation imposed by the level of $[Cu^{2+}]_{total}$. Additionally, the type of equation (see appendix 1) to construct the speciation diagrams can

be resolved from the AAS data: the comparison of the data obtained from the ISE measurements with the calculated results give an indication of how well the speciation calculation is coping with that great unknown, the soluble organic component of the solution.

In all cases, the pH measured in the supernatant was lower than that in the suspension eg. for Caprington, initial Cu = 0;

pH slurry = 6.06

pH supernatant = 5.74

Hence, we would expect that the lowering of the pH leads to a lower $(Cu^{2+})_{free}$ measured. However, the findings with the Cu ISE belied such a simple hypothesis: in those soils which gave measurable Cu activities, despite the pH drop on filtering, Arkleston and Dunlop followed the expected pattern (as did FS, Cap and BA, but only qualitatively so as their readings were below the limit of detection of the ISE). AHZ and Dreghorn moved in the opposite direction (as did FA, below the detection limit) - clearly the pH is not the only influence on the measured activity.

Earlier in this work, the influence of filtering on heavy metal standard solutions had been examined and shown to have no effect. Additionally, measurements of I (ionic strength) were obtained;

(a). before and after 24-hour equilibrations

(b). on filtering: again, by conductivity measurements.

This time, no change could be discerned. Given this information, one of the reasons proposed to explain the observed differences is that the filtering of the solutions disrupts the equilibrium existing between the soil and the supernatant:

If we consider the following situation;

$Cu^{2+}_{(aq)} + RO^{-}_{(s)} <=> (CuRO)^{+}_{(s)} \qquad K_r = \Omega$

$$\Omega = \{(CuRO)^{+}\}/\{(Cu^{2+}).(RO^{-})\}$$

RO^{-} representative of a cation exchange site bound to the matrix of the filtering materials. The value of RO^{-} in the denominator of the above equation may be considered to be very large, relative to the amount of Cu^{2+} passing within its vicinity. Thus we might say that RO^{-} is invariant from its initial 'concentration' and thereby write that

$$\Sigma = \{(CuRO^{+})\}/\{Cu^{2+})\}$$

$$\text{where } \Sigma = RO^{-} \times \Omega$$

Thus the amount of complexed Cu is ultimately dependent on (Cu^{2+}) and that the species ratio is to all intents and purposes constant. If any other ions are present to any great degree, relative to Cu, then the absolute amount of Cu removed from solution will be depressed, but where $Cu:\Sigma$(other cations) is narrower, then filtering should lower $[Cu^{2+}]_{total}$: this is not likely at relatively high Cu (or Cd) levels, and would explain any removal of Cu^{2+} from solution on filtering. This, so far, considers $[Cu^{2+}]$ only; in evaluating the influence on the 'free' Cu, we will no doubt be dealing with a balance of parameters, between the pH and competing cation levels (such as Ca, Mg, Na or K). With the 5 soils mentioned, the proton activity has been the determining factor, whilst with the other 3, the presence of other ions seems to have been influential. For both Cu an Cd, comparison of AAS figures before and after filtering on Whatman no.40 filter papers shows that, in both flame and furnace situations, filtering exerts a minimal influence upon the total levels of these metals in solution. Thus we must conclude that the process is changing the distribution

of the various metal species. The separation of the solid and liquid phases is one of the most basic features of any batch equilibration procedure (and to a lesser extent in flow through systems) and more work is required to elucidate how the separation process affects species distribution, whether it be by gravity, suction or pressure filtering or by centrifugation.

3.3.2. Organic Matter Removal.

The influence of thermal removal of soil organic matter on the sorption of Cd and Cu by Ark, AHZ and FA is shown in figures 3.20. (a-c) and 3.21. (a-c) respectively. In all cases, the removal of the organic portion (regardless of how complete this may be - but it was noted that whilst all the FA extracts had been coloured, the filtrates of the ashed soil contained no visible colour) resulted in an enhanced removal of metal from solution (the reaction between the Arkleston soil and Cd being an exception). If the best fitting straight line on all the points on the ashed soil is taken, it is possible to obtain some impression of the order of magnitude of the influence of organic matter in maintaining solution levels of Cu and Cd (table 3.13.).

Figures 3.20. and 3.21. Influence of Organic Matter Removal on Cu and Cd Sorption.

Figure 3.20. Influence of Organic Matter Removal On Cu Sorption.

(a). Ark.

(b). AHZ.

(c). FA.

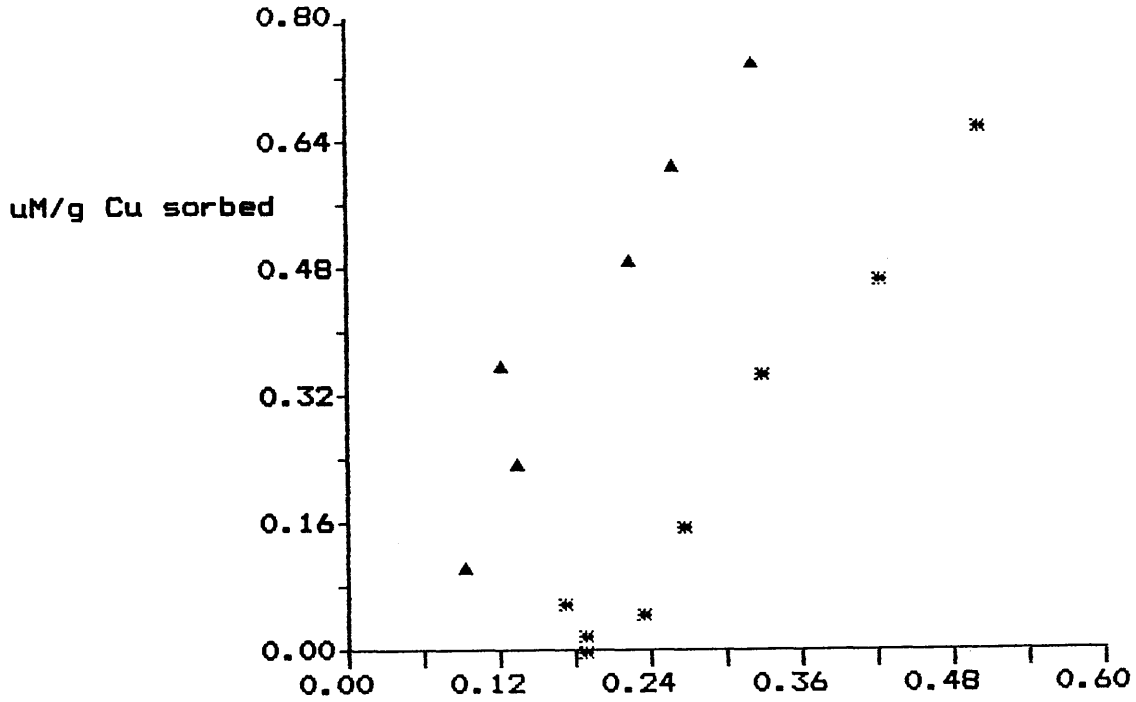
Figure 3.21. Influence of Organic Matter Removal On Cd Sorption.

(a). Ark.

(b). AHZ.

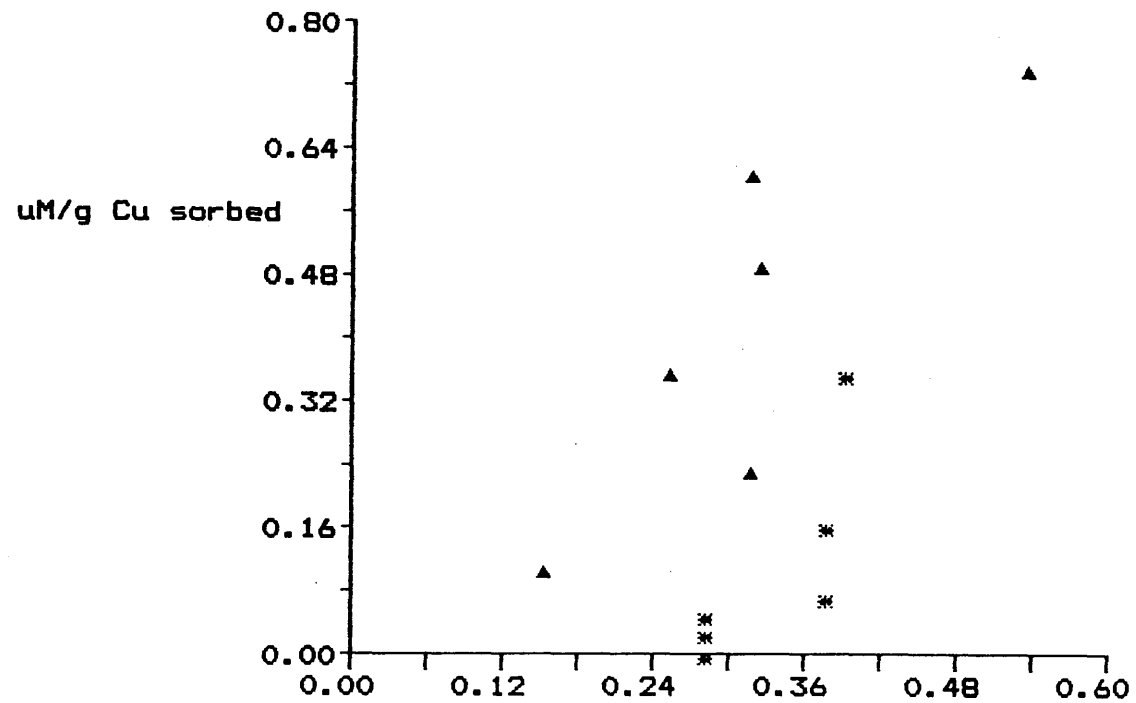
(c). FA.

a



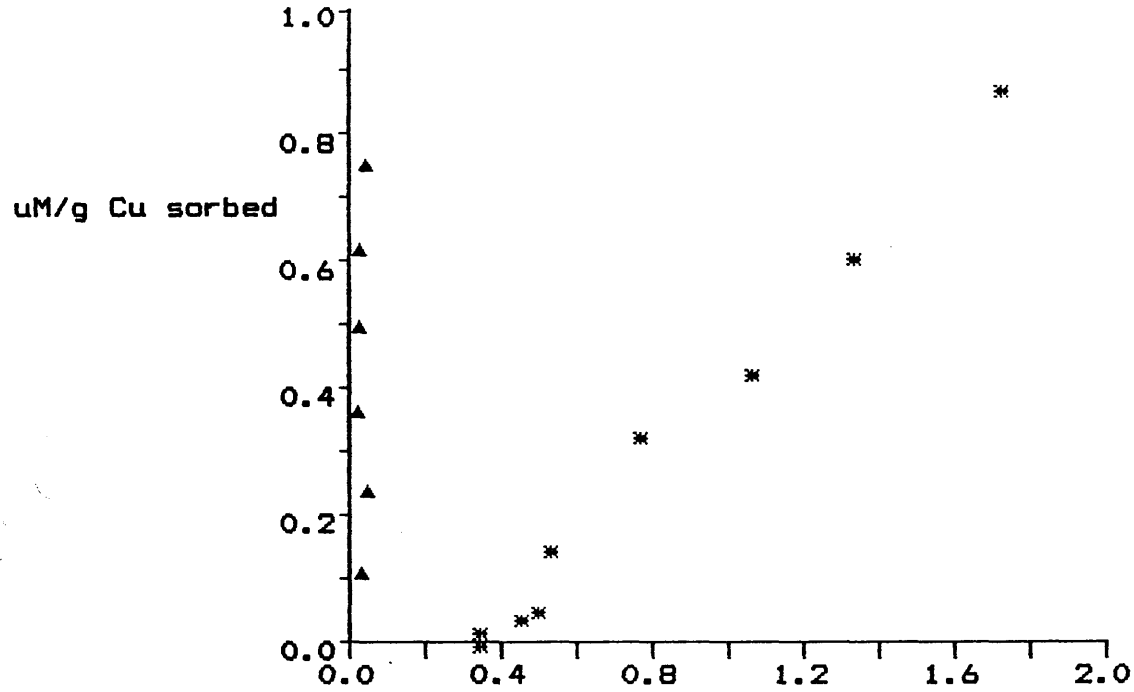
Influence of ashing on Cu sorption.
Air dry soil - * Ashed soil - tri.
ARKLESTON SOIL.

b



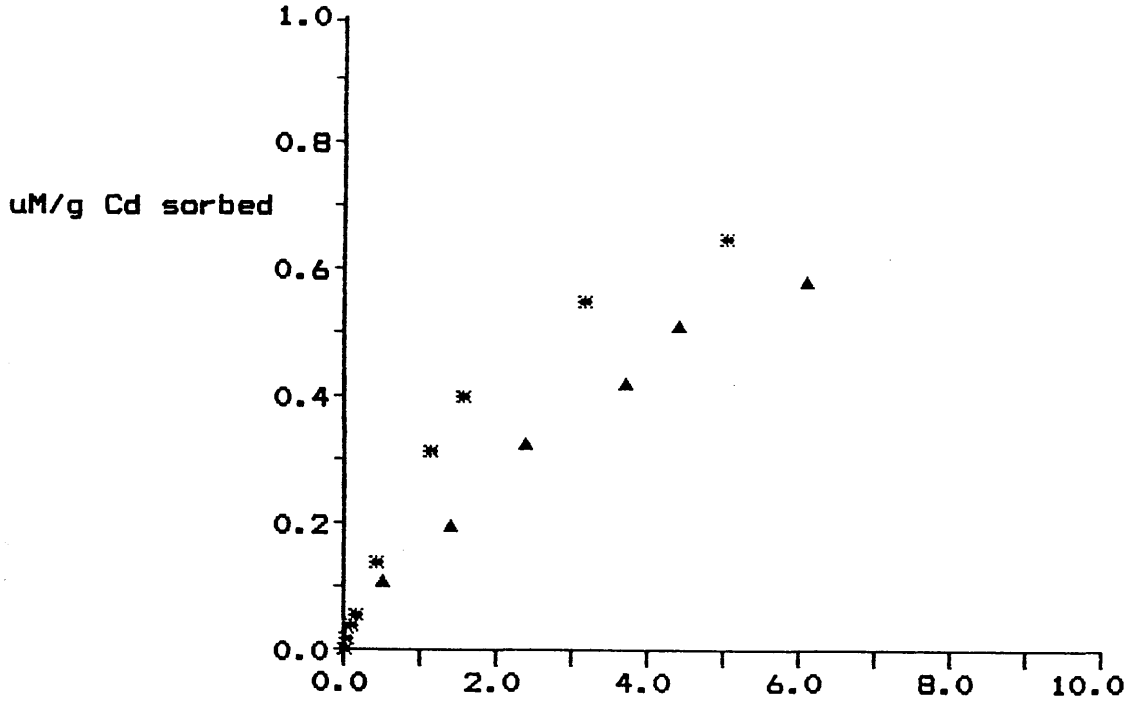
Influence of ashing on Cu sorption.
Air dry soil - * Ashed soil - tri.
ARKLESTON HIGH ZINC SOIL.

C



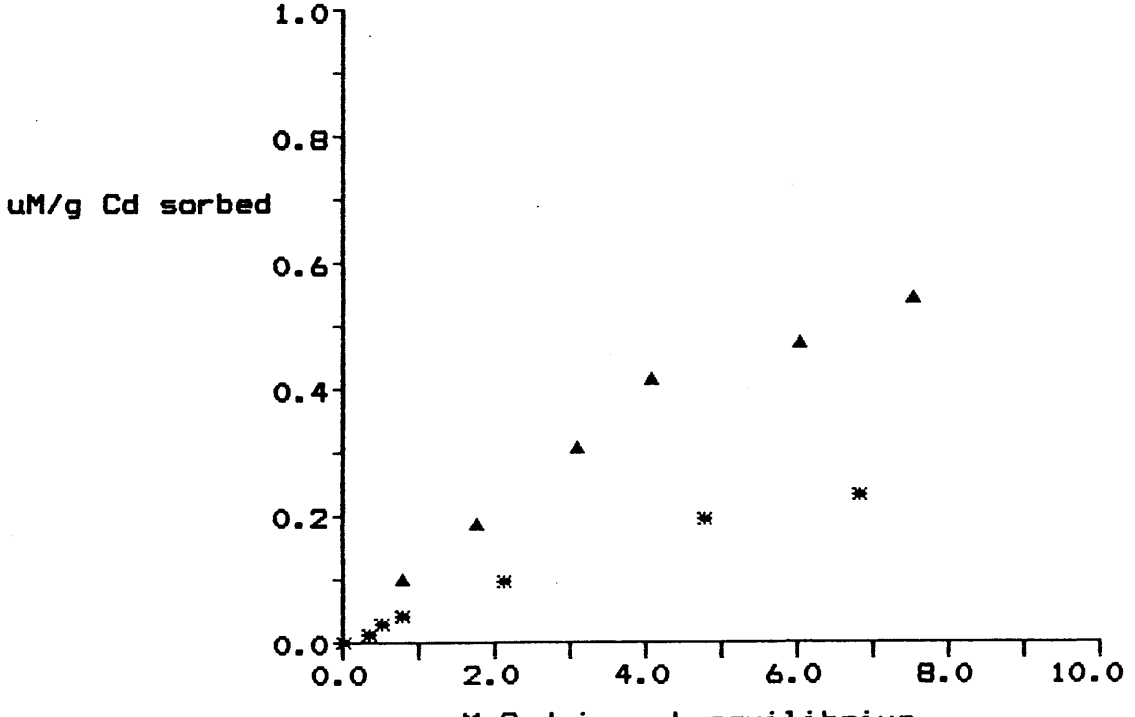
Influence of ashing on Cu sorption.
Air dry soil - * Ashed soil - tri.
FEN ARABLE SOIL.

a



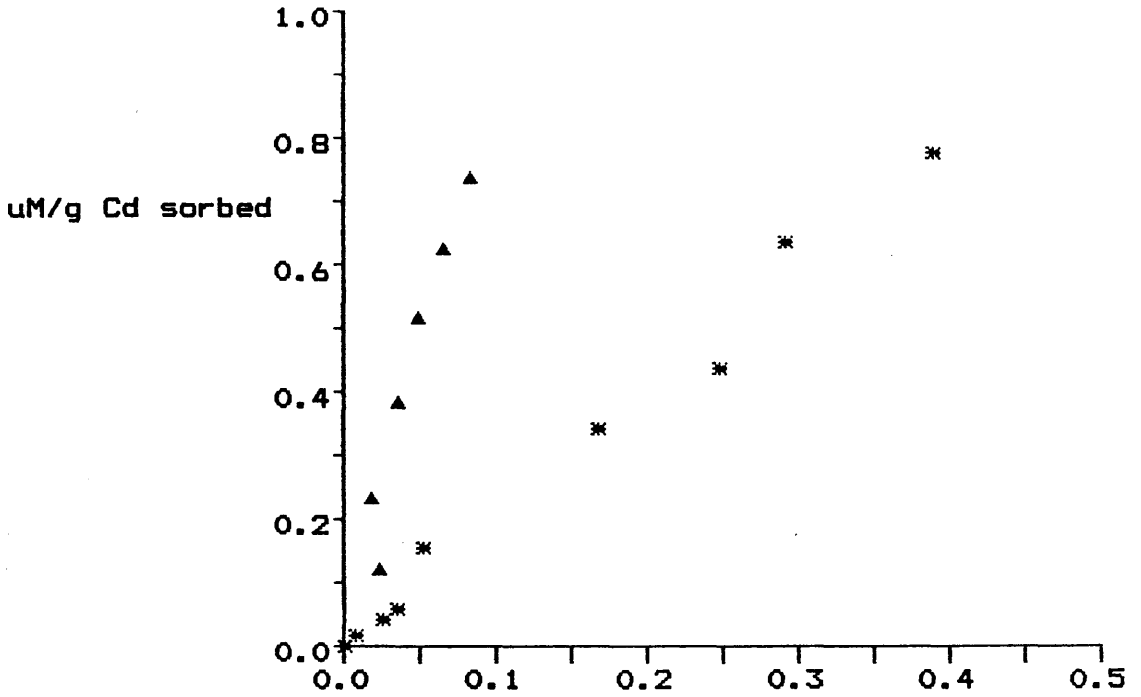
Influence of ashing on Cd sorption.
Air dry soil - * Ashed soil - tri.
ARKLESTON SOIL.

b



Influence of ashing on Cd sorption.
Air dry soil - * Ashed soil - tri.
ARKLESTON HIGH ZINC SOIL.

C



Influence of ashing on Cd sorption.
Air dry soil - * Ashed soil - tri.
FEN ARABLE SOIL.

Table 3.13. Gradient Changes: Ashed v Whole Soil.

	Ashed		Whole	
Soil-Element	Gradient	Intercept	Gradient	Intercept
Cu-Ark	2.543	-0.070	1.741	-0.287
Cu-AHZ	1.615	-0.094	0.377	-0.033
Cu-FA	14.075	0.408	0.278	-0.094
Cd-Ark	0.087	0.084	0.253	0.008
Cd-AHZ	0.065	0.082	0.033	0.011
Cd-FA	8.907	0.013	1.995	0.000

The factors of increase in the gradients are;

	Cu	Cd
Ark	1.46	0.34
AHZ	4.28	1.97
FA	50.63	4.46

This increased uptake is greatest for the Fen soil, which would correspond with the belief that the high pH of this soil leads to a high level of soluble organic matter which maintains levels of metals in solution rather than allowing them to be sorbed. Hence, the removal of such materials permits more of the ion to be sorbed on to surfaces - certainly, the S-shaped Cu isotherm of the whole soil is lost upon ashing, an effect also noted by Neal and Sposito (1986) for Cd.

The magnitude of the effect is greater for all soils with Cu rather than Cd, which serves to highlight the relative importance of the soluble organic fraction in the equilibrium behaviour of Cu. Indeed, in one case, the Arkleston soil, the effect of removing the organic component is to diminish the amount of Cd taken up on to the soil. This implies that the Cd was being taken up on to the soil-bound organic sites, and/or that ashing has so

altered the mineral component of the soil that uptake was reduced. Gadde and Laitinen (1974) have demonstrated this contrasting behaviour of oxide materials on ageing: doing so in the presence of metal leads to enhanced uptake, whilst doing so before introducing metal to the system results in reduced sorption. Shuman (1977) also showed that, for zinc, the thermal ageing of Goethite and Gibbsite reduced metal uptake 10-fold, which corresponded to the reduction in the surface area and CEC of the oxide (effectively by dehydration). Eriksson (1988) has presented data which show the influence of total soil organic matter levels on Cd retention and found, as with the Arkleston soil, that an increase in soil organic matter resulted in increase in the amount of Cd retained by soils.

In the previous section (3.3.1.2.), the relationship between pH and soluble organic matter was discussed. A further dimension to this argument is the direct influence which the organic matter has on pH in terms of the acid and base functions borne by such materials. Relative to the whole soil, the pH of the ashed portions were quite different: taking the average pH for the ashed soils (supernatants);

Ark Cd (6.08) > Cu (5.24) > Whole soil (4.25)*

AHZ Cd (5.70) > Cu (5.50) > Whole soil (4.28)*

FA Cu (7.77) > Cd (7.28) ≈ Whole soil.(7.30)*

*pH level in 0.1M $NaNO_3$ only.

In all instances, the removal of organic matter diminished the acidity of the system, which would enhance the uptake of metal ions, if it is assumed that such an effect leads to the increasing of the surface negative charge. Shuman (1988) found that the removal of organic matter, in one instance, resulted in enhanced Zn retention.

This may be evidence of a more complex balance of forces controlling the sequestration of metals in soils, in this case soluble OM v Bound OM v pH. The rise in pH of the Arkleston Cd system may not even have been large enough to counteract the reduced availability of organic sites (*cf.* Eriksson (1988) and Huaiman (1988)).

As pointed out by McLaren and Crawford (1973b), up until pH 6.0, Mn oxides have far higher Cu sorption capabilities than organic matter or Fe oxides. The heat removal of organic matter would tend to leave more Fe and Mn surfaces with their well-documented high affinity for Cu, exposed, although in a more crystalline form (with the negative effect this may have on sorption as pointed out by Gadde and Laitinen (1974) in mind). Kinniburgh *et al* (1976) have also demonstrated a very high affinity of oxides of aluminium and iron for Cd and Cu, and Spevackova and Kucera (1989) have, by a sequential extraction procedure, stated that most soil Cu resides in the oxide and residual pools ie. the mineral portions

.The work of Papodopoulos and Rowell (1988, 1989) and McBride (1980) has clearly exhibited the high degree of interaction between $CaCO_3$ surfaces and trace metals, most notably for Cd. Thus one might expect that the removal of organic material from soils, whilst eliminating many CEC sites and some specific organic sites, may reveal surfaces which, in alliance with the higher pH values recorded, could demonstrate a very high degree of interaction with the metals in question, higher indeed than in the whole soil. This would appear to be the dominant factor in five of the six systems studied here. If we compare the EDTA and oxalate extractable figures of Cu and Cd from tables 2.2. c and d respectively are compared, then it can be seen that the EDTA extractable Cd is 1/6 of the oxalate-extractable

fraction in the Arkleston soil, whilst it is undetectable in the Fen soils organic fraction (EDTA-extractable), but is present in the mineral fraction (oxalate-extractable). In the AHZ soil, the oxalate-extractable Cd is less than that removed in the EDTA extraction - this may be due to the high levels (relatively) of Cd and Zn, possibly precipitating as oxalates. From this, one might suggest that in the absence of organic matter, for the Ark, AHZ and FA soils, uptake of Cd will be enhanced. As this does not happen with the Ark soil, and as its pH rose quite markedly on ashing, it is suggested that the inorganic component of the soil underwent such a change on thermal treatment that its affinity for Cd was reduced.

For Cu, the split between the organic and inorganic fractions is $\approx$ 1:2 for Ark and 1:1 for AHZ. The Fen soil occupies the position of having most of its Cu bound into the organic fraction: despite this, the soil demonstrates quite a massive increase in the level of Cu sorbed upon removal of organic materials. The organic matter may have been blocking the oxide sites - the levels of Fe (see data tables from previous section in Appendix 2) certainly show parity with those of the soils containing no native Calcite: as pointed out by Greenland and Mott (1978), the humic and fulvic fractions of soil are most commonly found associated with the hydrous oxides of iron and aluminium.

3.3.3. Influence of Initial pH.

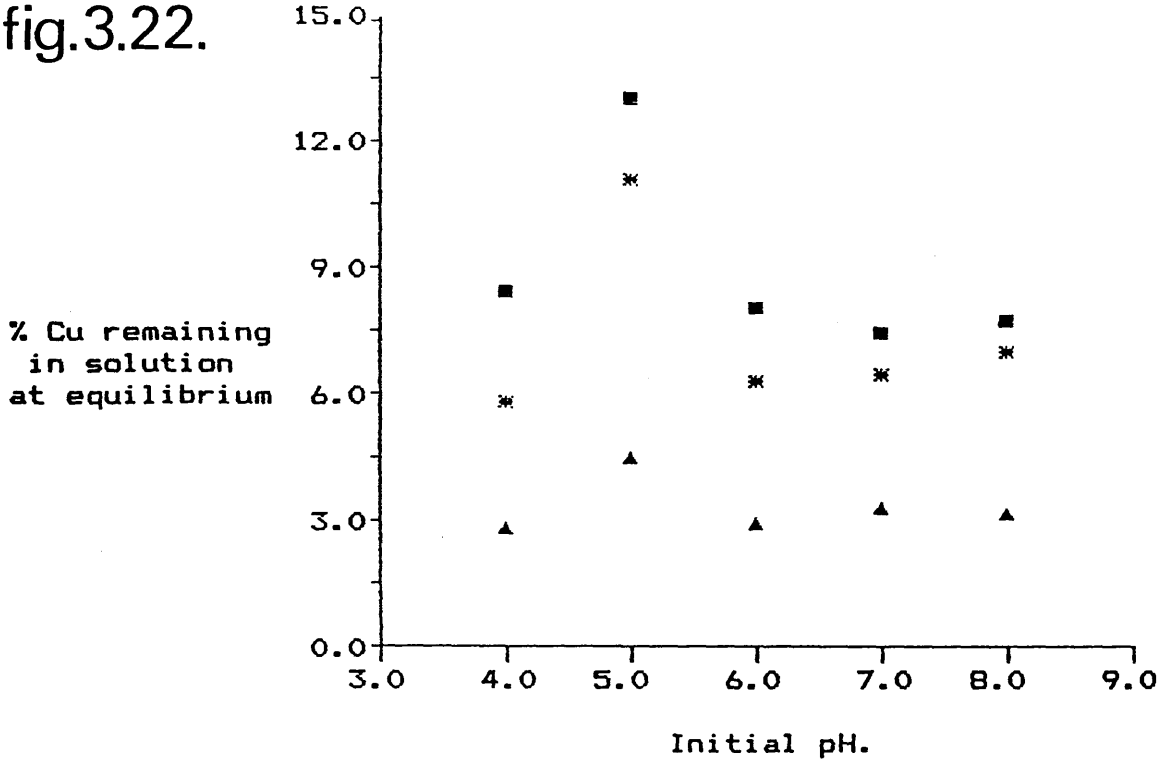
In section 1.2.3., the relative pH sensitivity of Cu and Cd speciation in 0.1M $NaNO_3$ was examined. Up to ≈ pH 6.0, the 'free' Cu^{2+} ion predominated, whilst this range could be extended to pH8 for Cd: both in the absence of any organic ligands. Thus, it would be expected that very small differences in uptake due to inorganic speciation would be found over the normal pH ranges of soils (the graphs pertaining to this data are presented in figures 3.22. and 3.23.).

Figures 3.22. and 3.23. Influence of Initial pH on Cu and Cd Sorption.

Figure 3.22. Influence of Initial pH on Cu Sorption.

Figure 3.23. Influence of Initial pH on Cd Sorption.

fig.3.22.



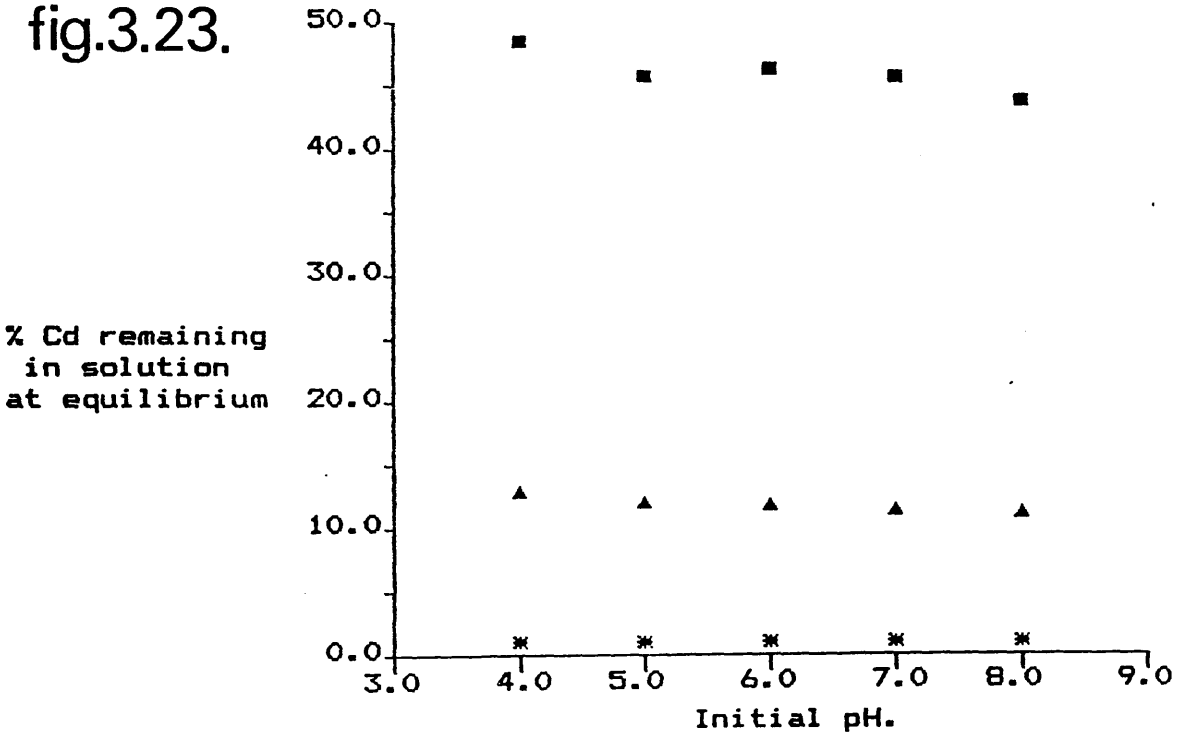
Effect of initial pH on Cu remaining in solution.

ARKLESTON - tri. ARKLESTON HIGH ZINC - sq.

FEN ARABLE - *.

Initial Cu concentration = 15uM.

fig.3.23.



Effect of initial pH on Cd remaining in solution.

ARKLESTON - tri. ARKLESTON HIGH ZINC - sq.

FEN ARABLE - *.

Initial Cd concentration = 15uM.

This is what is found with the Ark, AHZ and FA soils: despite the initial pH of the equilibrating solutions of Cd an Cu being set to pH 4, 5, 6, 7 and 8, the differences in the amounts of Cd and Cu sorbed at each pH are very small. The Cd figures show a very gradual increase in the amount of metal being sorbed, whilst with Cu, the Fen and Arkleston soils show an increase in solution metal levels (the AHZ situation is less clear, but could show a turning point). All three soils exhibit a sharp peak at pH 5 for the Cu systems, which, given that post equilibration the pH's of the supernatants varied little from those of the non-poised systems, is difficult to ascribe to anything other than a systematic error in the experiment. This lack of influence of the initial pH upon the final level of Cu in solution has been noted by Jarvis (1981), albeit in a system which involved adjusting the pH of the suspension following addition of the Cu. Likewise, McLaren et al (1981) stated that through the normal pH range of British soils (5 - 7), pH exerted little influence upon the removal of Cu from solution by either humic acid, a soil oxide or Montmorillonite. However, this lack of effect has been shown for $[Cu2+]_{total}$, McBride and Blasiak (1979) measured $(Cu^{2+})_{free}$ by ISE and showed that whilst $[Cu^{2+}]_{total}$ actually demonstrated an increase > pH 6 - due to enhanced solubility of organic matter (an effect also noted by McLaren et al (1983) and Kuo and Baker (1980)), $(Cu^{2+})_{free}$ continued to fall linearly with pH. Where Cd is concerned, the small rise in the percentage sorbed with pH is in agreement with the findings of Garcia-Miragaya and Page (1978), Soon (1981) and Christensen (1984), although not to as high a degree.

3.4. Overview of Chapter 3.

The principal observations which can be made about the findings of this chapter are as follows;

(a). The level of Cd or Cu addition is important in determining how the soil will react.

(b). Soluble organic matter plays a major role in the low level solution chemistry of Cu.

(c). At the levels of metal examined, mineral solubility can be discounted as the means which regulates the amounts of the two metals in solution.

(d). The absence of pH, Mn, Fe or Ca changes which can be unequivocally linked to uptake of Cd or Cu, and the high level of $NaNO_3$, imply that the low level sorption of these metals is by way of very specific sites. Allied to this is the lack of any correlation between the common soil properties and any of the uptake parameters.

(e). Surface bound organic matter can act to hinder metal uptake, both in terms of its acting as a reservoir of soluble organic material and in the way it can physically obstruct mineral sites. This leads to the conclusion of a very great role in uptake for oxides and carbonates - indeed, in only one instance, for Cd , was bound organic matter aids metal removal from solution.

(f). The initial pH of a solution coming into contact with a soil has little influence on the uptake of Cd and Cu: general trends could be said to be increased sorption of Cd with pH, whilst that of Cu declines.

(g). Data summation can be achieved most simply via the van Bemmelen-Freundlich equation, which is almost completely linear over several orders of magnitude for Cd. Copper uptake, too, is well described by the above equation - the curvature lends itself to splitting into two segments,

each described by straight lines.

Chapter 4. Competitive Influences on Sorption.

4.1. Cationic and Anionic Modifications to the Soil Retention of Copper and Cadmium.

The previous chapter concentrated upon the uptake of the two metals copper and cadmium from a solution which contained a relatively high level of $NaNO_3$. The reasons used to justify the inclusion of such a compound were;

(a) to aid ISE measurements

(b) to exclude any non-specific soil-solute interactions.

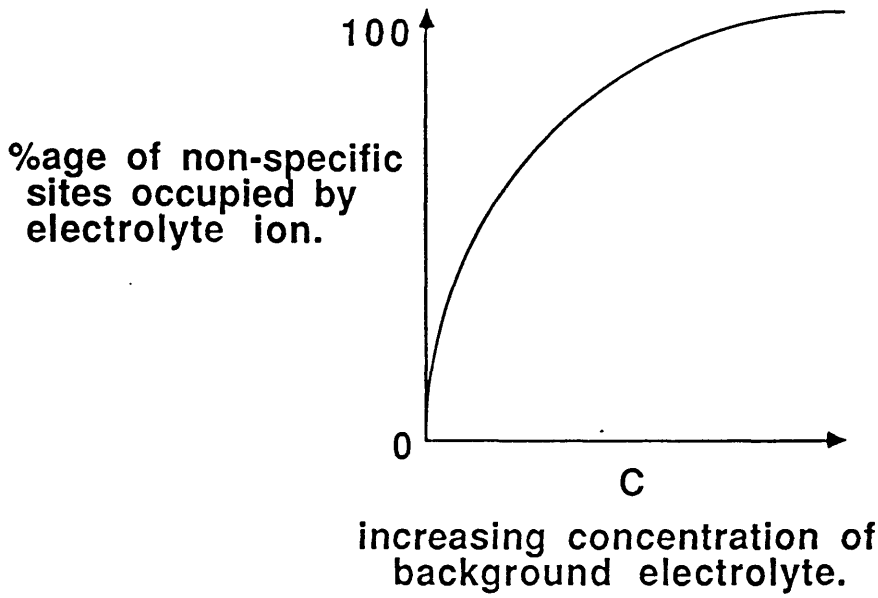
In stating the second reason, it has been accepted that there will be some degree of competition between the components of the bulk solution and the portion which it is intended to study: indeed all studies of cation or anion interaction with surfaces, where conducted in a background electrolyte are, essentially, competitive systems, whether that is from the presence of the cation or the anion, or indeed, both. Simply by considering the implications of mass action, the presence of a high activity of a cation or anion will "force" the equilibrium of the sorbent-sorbate to the sorbed side ie.

$$Y^-/X^+ + \text{Surface} \quad \text{(Surface - } X/Y^-\text{)}$$

$$\longrightarrow \text{ Increased by mass action.}$$

In choosing to use a background electrolyte, it is hoped that only this sort of competition with the chosen cations will occur, and that the concentration used is sufficient to push this almost to completion: we might visualize the effect thus (Figure 4.1.).

figure 4.1. Influence of background electolyte concentration on availability of non-specific sites.



Two principle cations are chosen as background components, sodium and calcium. Calcium is employed at lower concentrations than sodium and is thought to be particularly of use in divalent metal ion studies as it blocks sites of low specificity which may have been targets for these ions: it is presumed that at high enough Na concentrations, the influence will be much the same. In terms of their influence on the solution organic chemistry, the two cations have very different influences: Na^+ tends to disperse organic material (as well as the inorganic soil colloids), whilst Ca^{2+} acts as a flocculant. This effect is clearly demonstrated in the work of Kuo and Baker (1980). Thus, it becomes difficult to compare work conducted in different background salts (a way round this would be to deal in activities all the time, but noted in the previous chapter, the reliability and detection limits are insufficient to be applied at the low levels found in real systems and in low level metal loading studies).

The anion included in these studies is also of crucial importance in terms of its ability to complex Cu and Cd. In section 1.2.3 the influence of NO_3^- and pH on the speciation of Cu and Cd was documented: the choice of NO_3^- as a background anion is justified by the fact that it shows little ability to complex with either Cu or Cd. Other commonly used anions are the Perchlorate (ClO_4^-) and chloride ions, chosen for their low complex and ion-pair forming tendencies; the Cu and Cd stability constants for some commonly used anions and Cu and Cd are given in table 4.1.

Table 4.1. Some Cu and Cd Stability Constants.

	NO_3^-	Cl^-	SO_4^{2-}	ClO_4^-
Cu	0.5	0.40	2.36	-17.2 *
Cd	0.31	1.98	2.45	no value available

(all from Lindsay, 1979 except * from Smith and Martell, 1976)

Few reports have appeared in the literature examining the role of inorganic anions in equilibrium studies; far less have been published in connection with the part organic liquids play in these schemes: a summary of some author's findings is given in Table 4.2., with respect to inorganic ions [in this table, mobility is equated with reduced uptake]. Additionally, Elrashidi and O'Connor (1982) found that ionic strength and anions (NO_3^- ,Cl^- and SO_4^{2-}) had no influence upon zinc uptake on to soils, whilst Kuo (1986) demonstrated no interaction between cadmium and phosphate in relation to sorption on to hydrous ferric oxide.

Thus, it can be seen, that despite the thermodynamic evidence that complexation by inorganic ligands should influence metal-solution-solid relationships, the real situation is by no means so clear cut.

Table 4.2 Mobility Sequences for Inorganic Anions

Metals	Order of increasing mobility	Reference
Cu, Cd	$Cl^- > ClO_4^-$	Doner (1978)
Cd	Cl (a) $> Cl$ (b) $> ClO_4^- > SO_4^{2-}$	O'Connor *et al*, (1984)
Cd	$Cl^- > ClO_4^- \approx SO_4^{2-}$	Garcia-Miragaya & Page (1976)
Zn	$Cl^- \approx NO_3^- > SO_4^{2-}$	Shuman (1986)

(a). = 0.10M (b). = 0.01M.

Neal and Sposito (1986) have indicated the effect organic molecules in solution can have on Cd retention by soils and Mench *et al* (1988), isolating low molecular weight root exudates demonstrated that these could readily sequester heavy metals, including Cu. Using a Cu ISE, Cavallaro and M^{c}Bride (1978) showed that conditions which favour solubilization of organic matter (high organic matter, high pH) gave low Cu^{2+} activities compared to the total Cu figures. Little evidence of a similar set of conditions for Cd could be shown, this could concur with the findings of Stevenson (1977), who demonstrated log K values for Cu humic extract complexes at least two orders of magnitude greater than those for Cd.

The influence of cations upon the removal of Cu and Cd has been studied little more than for anions. The influence of one, the proton has been discussed (in terms of pH) in the

previous chapter. This chapter will focus upon some of the other soil cations to monitor their effect upon Cu and Cd uptake. Given that the stability constants for some metal-anion complexes can be quite substantial (as previously noted), it may be difficult to extricate the cation influence from the whole salt influence at the macro level; ie. in the study by Petruzzelli *et al* (1985), increasing concentrations of $CaCl_2$ were shown to markedly decrease the amounts of Cu and Cd sorbed by the soil. Christensen (1984) examined the influence of Ca upon Cd removal from solution and found that in a background electrolyte of $CaCl_2$, even when ion-pairing has been taken into account, a ten-fold increase in the concentration of $CaCl_2$ led to diminished Cd retention by soil: distinct evidence of high level competition. Gaszczyk (1988) examined the effect of liming upon the extractability of several heavy metals and found that the pH increase induced by liming resulted in a reduction in the ability of Mg, Ca, Ba, K and NH_4^+ to displace Cu from the soil complex. Conversely, NH_4^+ and Ba^{2+} showed increased potential for Cd^{2+} exchange (a slightly curious point shown by this work is that, despite the oft quoted similarity in their ionic radii, the competition between Cd and Ca is less that that between Cd and Mg). In terms of their ability to depose other cations, the following sequences were deduced;

$$Cu: Mg \geq Ba > Ca > NH_4^+ > K$$

$$Cd: Mg > Ca > Ba > NH_4^+ > K$$

$$\longrightarrow$$

Decreasing Competitive Effect

Lagerwerff and Brower (1972) looked at the uptake of Cd as influenced by the chlorides of Al, Ca and Na (at lowest, in approximately 50 times excess of the Cd used). Ion-pairing

was not considered, but Al and Ca did show an ability to reduce Cd uptake. Na displayed somewhat anomalous behavior in that Cd^{2+} uptake decreased as, up to a point, the Na^{+} concentration decreased, whilst pH rises (a possible explanation, not explored in this paper, is the dispersion of organic matter by Na^{+} and increasing soluble organic matter resulting in higher than expected solution concentrations of Cd).

Christensen (1987a) commented on the dearth of information regarding the way(s) in which heavy metals interact in soils: this is of particular importance given that municipal and industrial wastes, slurries and manures will not contain just one metal, but varying levels of contaminants. His studies have involved examining the influence of heavy metals (as found in the above named waste materials) on the sorption of Cd. The major finding from this work (and a subsequent paper Christensen ,1987b) develops this theme) is that Zn competes most effectively with Cd: in fact, a combination of Zn, Co and Ni competed with Cd to the same extent as Zn on its own. A mixture of Cu, Cr and Pb was also shown to reduce Cd uptake, sometimes more effectively than Zn. In this paper (Christensen 1987a), the initial levels of addition of the competing ions, relative to the Cd concentrations are not given, but at equilibrium, there is approximately a thirty-fold excess (in Molar terms) of Zn over Cd. Kurdi and Doner (1983) looked at Zn-Cu interactions and found, for a single level of Cu, that Zn had very little competitive influence on Cu, implying independent, additive uptake. However, in a parallel series of experiments, Cu was found to vastly reduce the amount of Zn retained by soil. The conclusion one reaches from this is of a pool of sites which preferentially retain Cu, but in the absence of Cu, can

accommodate Zn. Elliott *et al* (1986) looked at the concurrent uptake of Cu, Cd, Pb and Zn on to soil. In the absence of individual uptake studies, assessment of a competitive effect cannot be performed, however, their findings demonstrated an order of affinity as follows; Pb > Cu > Zn > Cd, the latter two positions being reversed as the soil organic matter increases. In contrast to this M^{c}Bride and Blasiak (1979) noted that Zn and Cu uptake was additive at approximately 300 μM Cu: 600 μM Zn.

A further way of examining a competitive system is to monitor the displacement of ions from surfaces on adding other ions to the system. The proton has, in this context, already been discussed. M^{c}Bride (1980), Davis *et al* (1987) and Papadopoulos and Rowell (1988) have all recorded the release of Ca when Cd is taken up by Calcite and Calcareous soils, at levels of Cd (equilibrium) of between 10^{-6} and 10^{-4} M. In a succeeding paper, Papadopoulos and Rowell (1989) also found that Cu^{2+} could displace Ca^{2+} from the same types of surfaces. Doner *et al* (1982) found that Cu, Cd and Ni could displace Mn (II) from ∂-MnO_2. Cu uptake released most Mn (II), and also most protons: the two events are probably linked, as in a further paper, Traina and Doner (1985 a and b) postulated the proton catalysed reduction of ∂-MnO_2 as being one of the principle pathways to Mn (II) release: not simply by M^{2+} <=> Mn^{2+} exchange.

With these observations in mind, a series of investigations was embarked upon, with a view to clarifying the position of cationic and anionic roles in the regulation of the solution chemistry of Cu and Cd.

4.2. Materials and Methods.

4.2.1. Cation Influence.

All of the data pertinent to this section can be found in appendix 3.

Three soils were chosen for this experiment: Arkleston, Arkleston High Zinc and Fen Arable, on the basis of range of pH, soluble organic matter and native presence of ions.

Two different approaches were used with Cu and Cd: in the trials observing the influence of other cations on Cd retention, three competitive levels of competing ion were used against a range of Cd concentrations, whilst with the Cu experiment, the level of competing ion was always poised, in Molar terms, to match that of the Cu.

The range of Cu and Cd studied involved ten concentrations: 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 μM, in 0.1 M $NaNO_3$. In the Cd experiments, the competing ions chosen were K^+, Pb^{2+}, Fe^{3+}, Zn^{2+} and Cu^{2+}, at levels of 5, 15 and 60 μM. The solutions were made up (0 - 30 μM) containing the above stated level of competing ion. Similarly, with the Cu system, dual-ion equilibrating solutions were constructed (with equivalent Cd^{2+}, Zn^{2+}, Pb^{2+} or Fe^{3+} and a combination of all four; K^+ was left out of this series as the results from the Cd experiments indicated that K^+ had a minimal influence on Cd^{2+} sorption. As Cd^{2+} has been suggested to reside mainly on CEC sites, which would be the chief destination for K^+, then the inability of K^+ to interfere with Cd^{2+} sorption would suggest that it would also have a very slight effect on Cu^{2+} uptake) with an additional three concentrations of 100, 200 and 300 μM. Fifty ml of each solution was used, with approximately 2.0 g of air-dry soil, shaken in plastic

bottles for 24 hours. The solution and supernatant were subsequently separated by filtration, collected in plastic bottles, and pH, Cu or Cd and competing ion determined immediately (AAS for all metals except K, for which AES was used).

4.2.2. Anion Influence.

All of the relevant data of this section can be found in appendix 4.

In all of the previous experiments NO_3^- has been the anion in the electrolyte. This set of experiments chose to examine the changes in the sorption pattern brought about by using chloride, sulphate and citrate: all with Na^+ as their counter-ion. In order to make a direct comparison, in activity terms, of these systems, the concentrations of these anions were chosen such that they would provide a background ionic strength of 0.1M. A development of this experiment was whether or not the observed differences were solely due to concentration differences: to this end, a series of experiments was also conducted in various concentrations of NO_3^-, again with Na^+ as the counter-ion.

Thus, using the same three soils as above, a range of Cd and Cu concentrations was examined (5, 10, 15, 20, 25 and 30 μM) in;

(a). 0.1000 M NaCl

(b). 0.0333 M Na_2SO_4.

(c). 0.0167 M Na_3Citrate.

50mls of solution was equilibrated for 24 hours with ≈2.0g of air-dry soil, in plastic bottles on an end-over shaker. Following this period the solutions were filtered and pH and metal concentrations were measured.

In the subsequent series of determinations, 3 soils were

used (as above) and the same Cd and Cu range was examined. In this instance, NO_3^- was the anion used, and sorption was monitored in 0.0333 and 0.0167 M $NaNO_3$ (the sorption figures for 0.1 M being available from the previous chapters' experiments). Filtering was succeeded by pH and AAS metal determination.

4.3. Results.

4.3.1. Cation Effects.

Cadmium

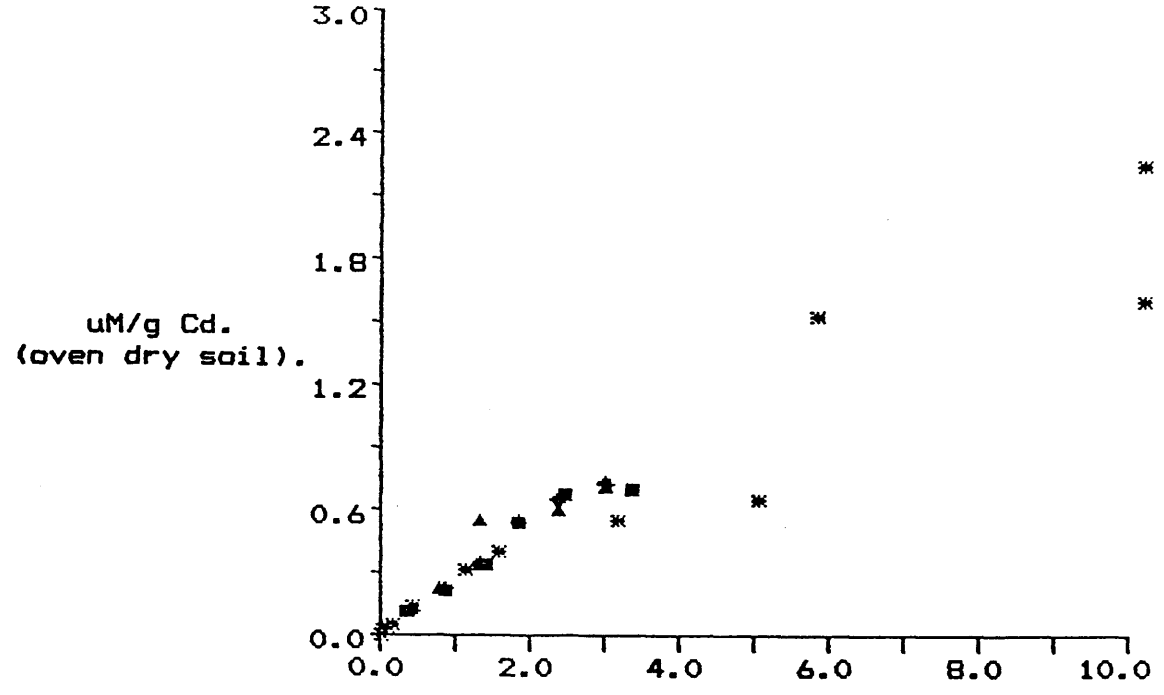
The graphs displaying the 3-tiers of competing ion competition upon Cd retention are shown in figure 4.2. (a-o). For comparisons sake, the sorption line from the previous chapter is included in each graph (uptake in 0.1 M $NaNO_3$ only).

Figure 4.2. Cd Competitive Isotherms.

Figure 4.2. Cd Competetive Isotherms

(a). Ark-K	(f). AHZ-K	(k). FA-K
(b). Ark-Fe	(g). AHZ-Fe	(l). FA-Fe
(c). Ark-Cu	(h). AHZ-Cu	(m). FA-Cu
(d). Ark-Pb	(i). AHZ-Pb	(n). FA-Pb
(e). Ark-Zn	(j). AHZ-Zn	(o). FA-Zn

a



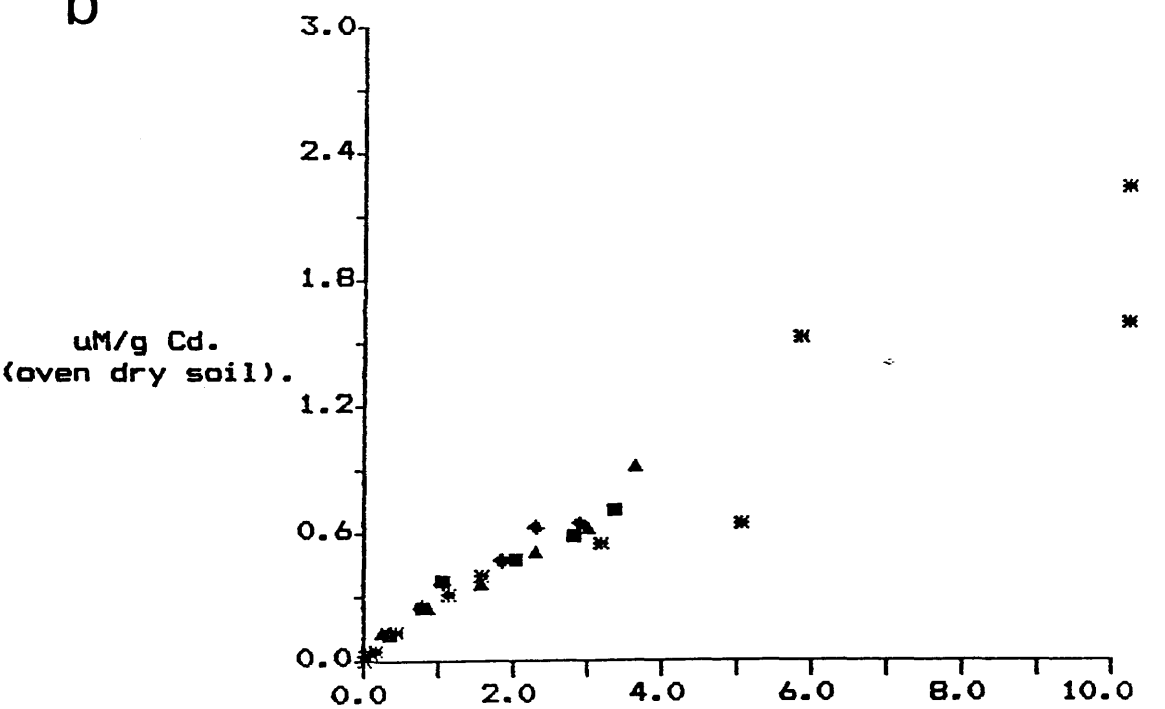
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v POTASSIUM, ARKLESTON.

b



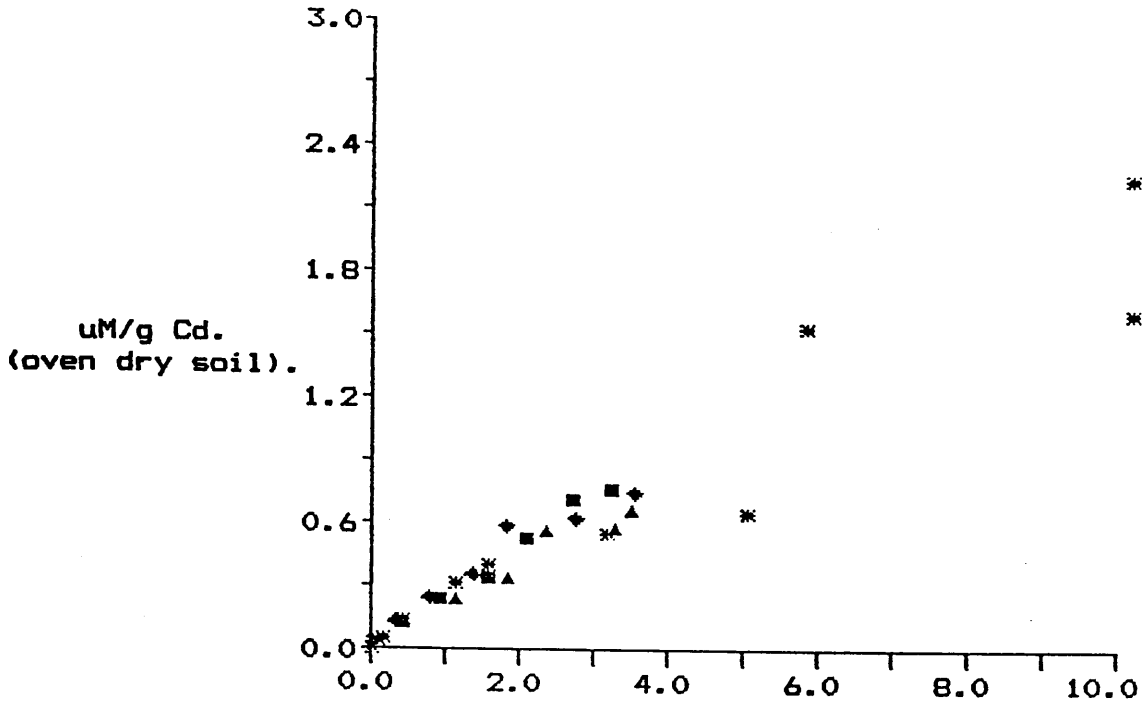
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v IRON, ARKLESTON.

c



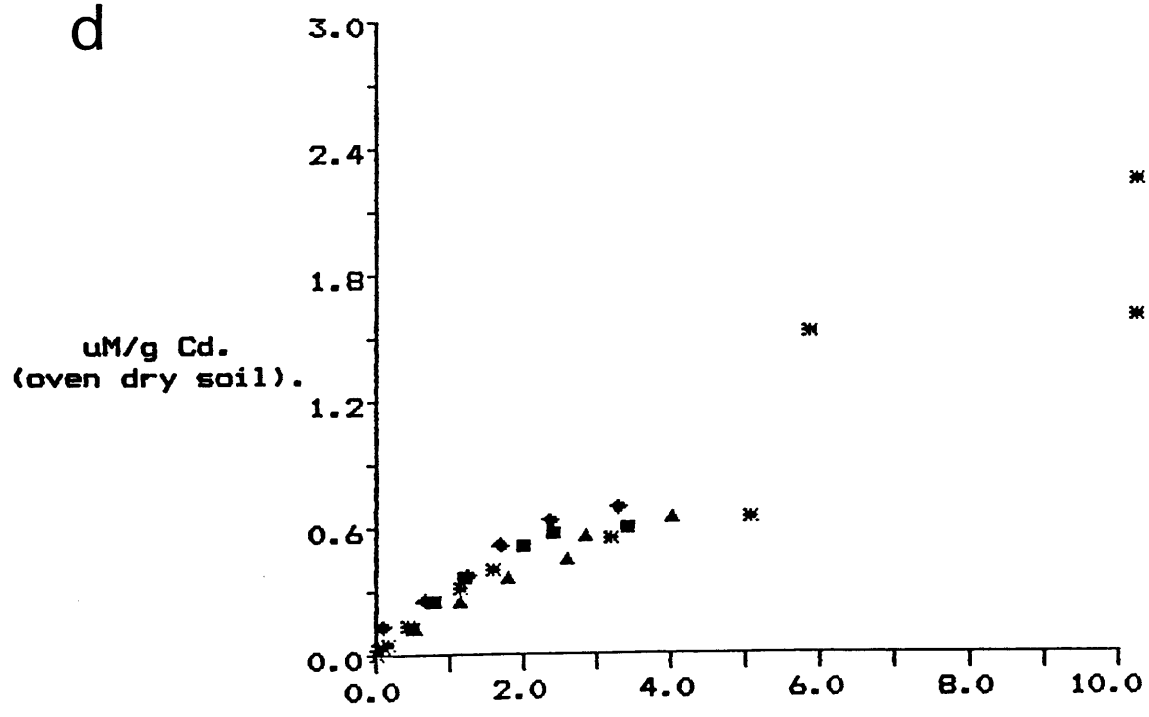
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v COPPER, ARKLESTON.

d



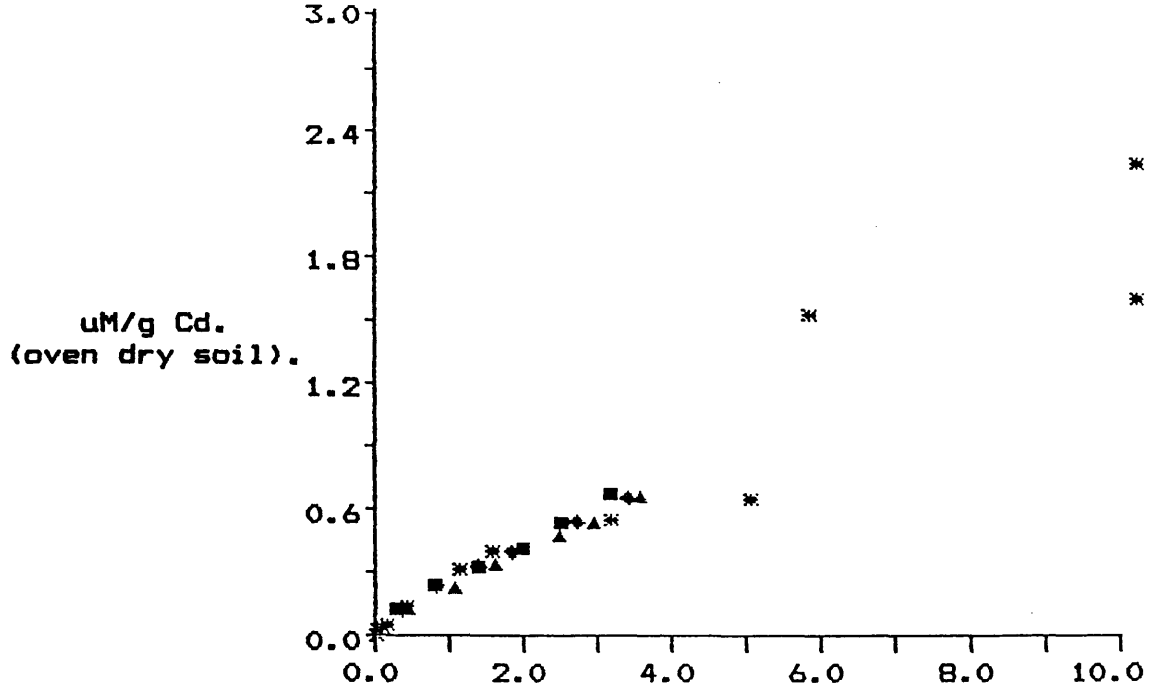
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v LEAD, ARKLESTON.

e



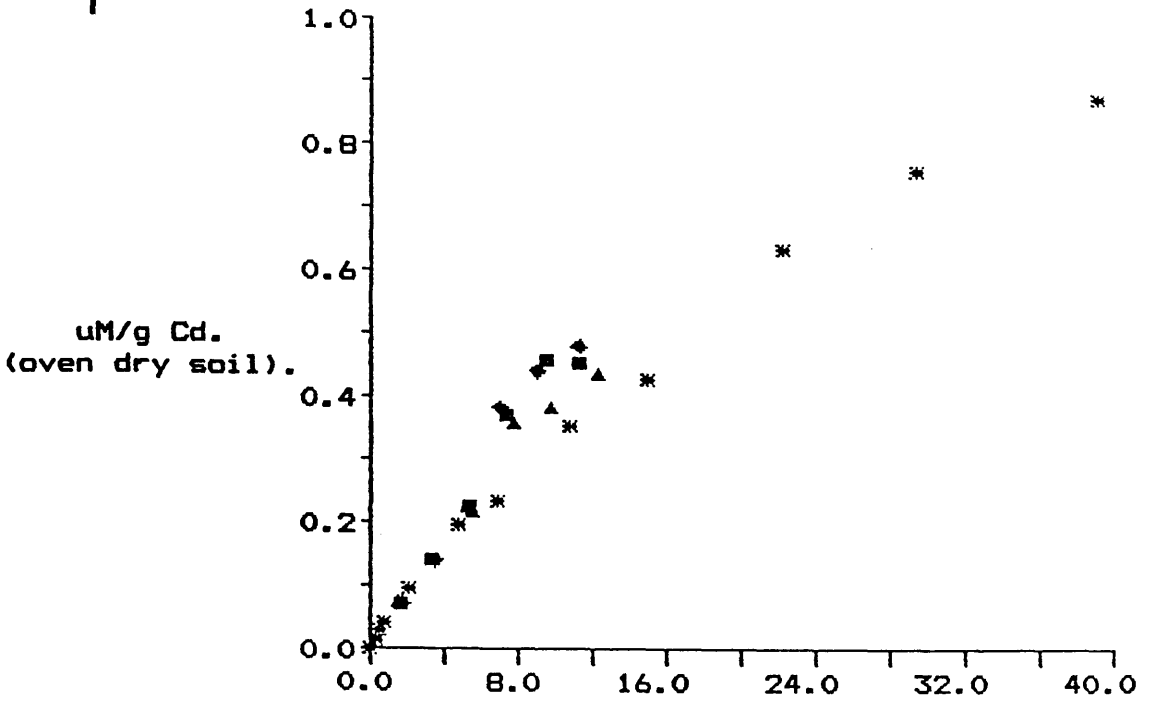
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v ZINC, ARKLESTON.

f



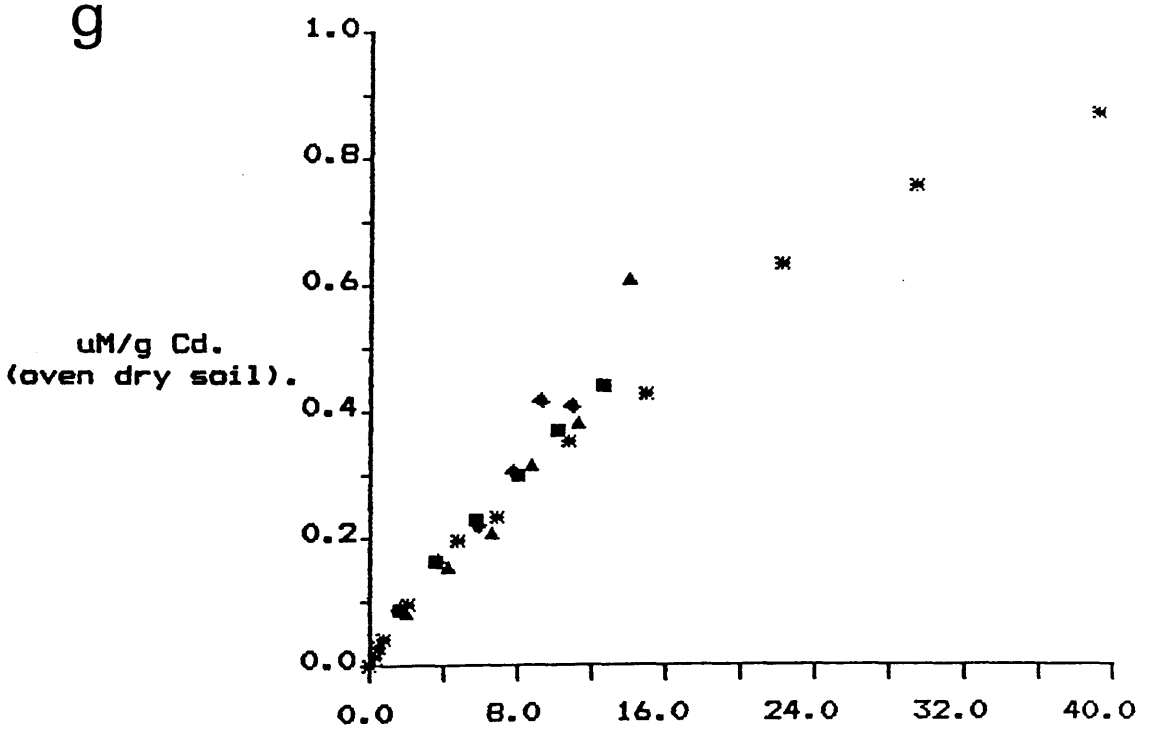
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v POTASSIUM, ARKLESTON HIGH ZINC SOIL.

g



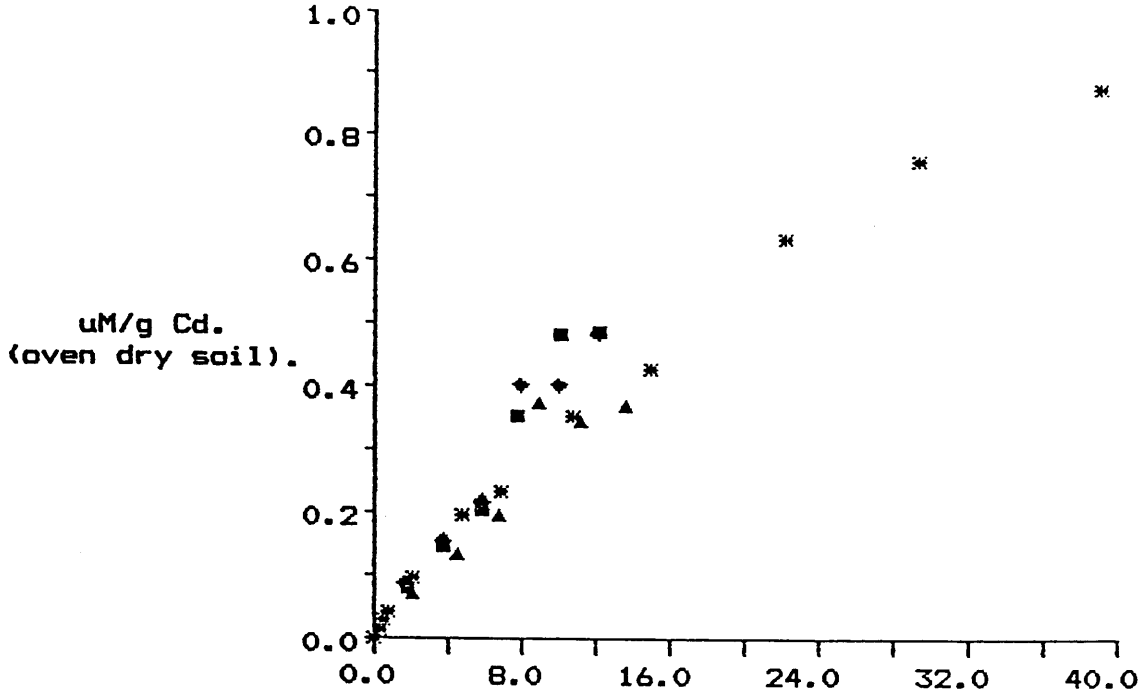
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v IRON, ARKLESTON HIGH ZINC SOIL.

h



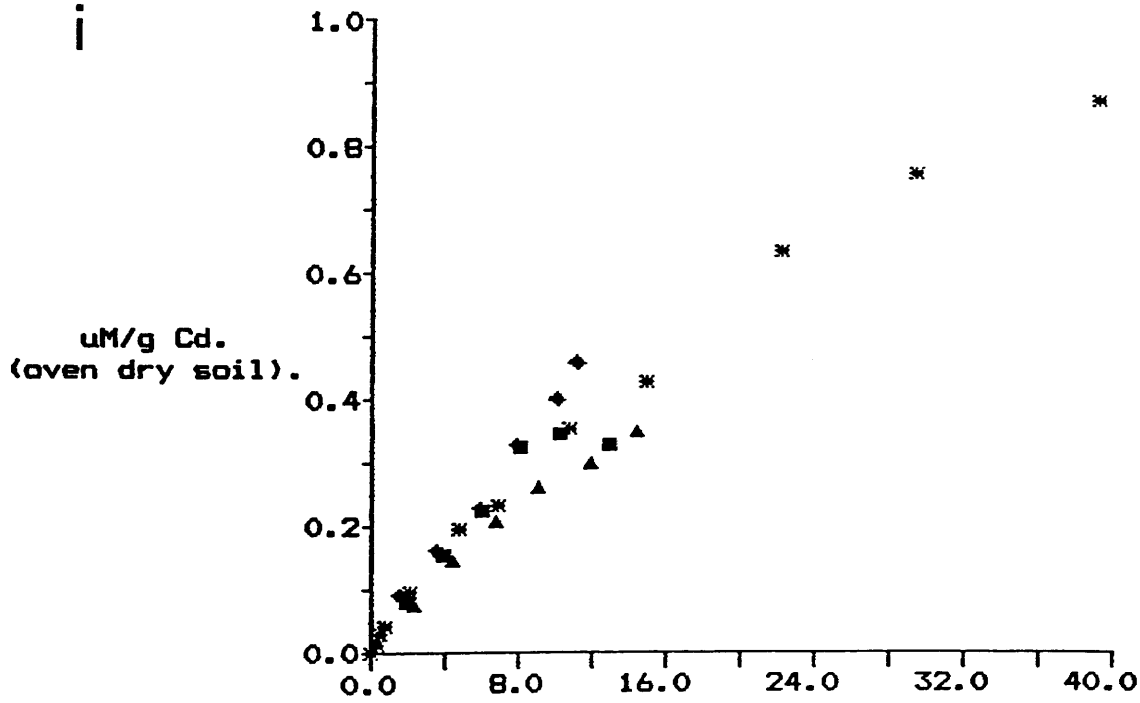
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v COPPER, ARKLESTON HIGH ZINC SOIL.

i



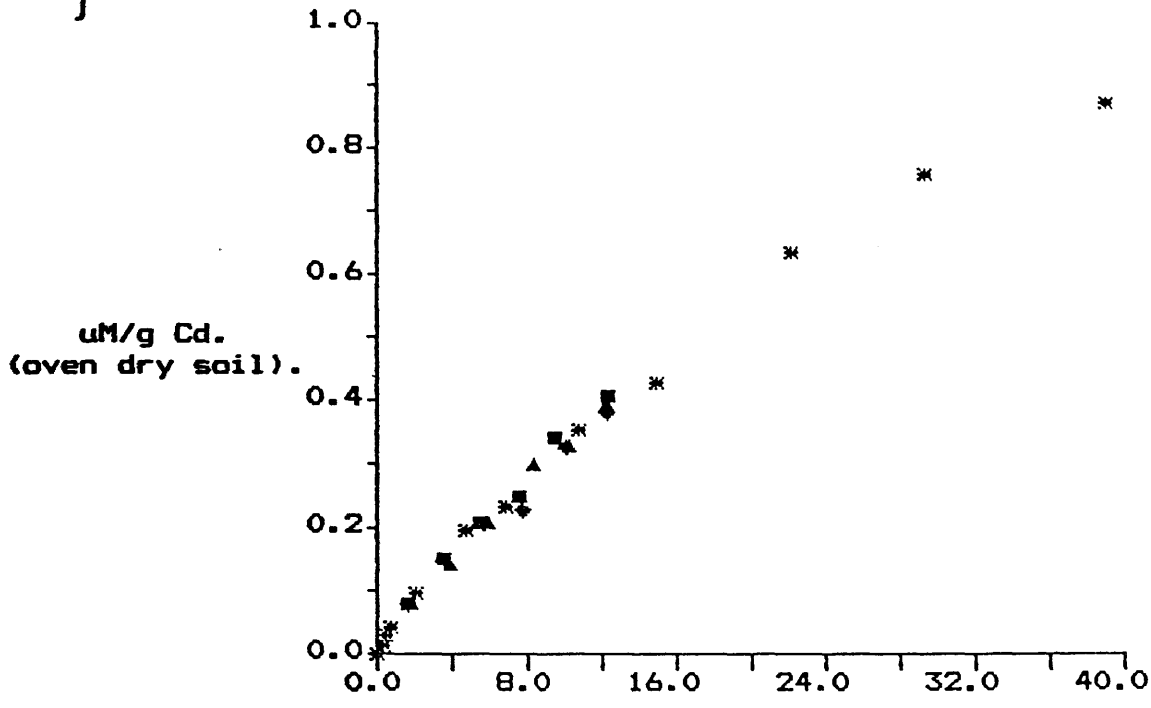
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v LEAD, ARKLESTON HIGH ZINC SOIL.

j



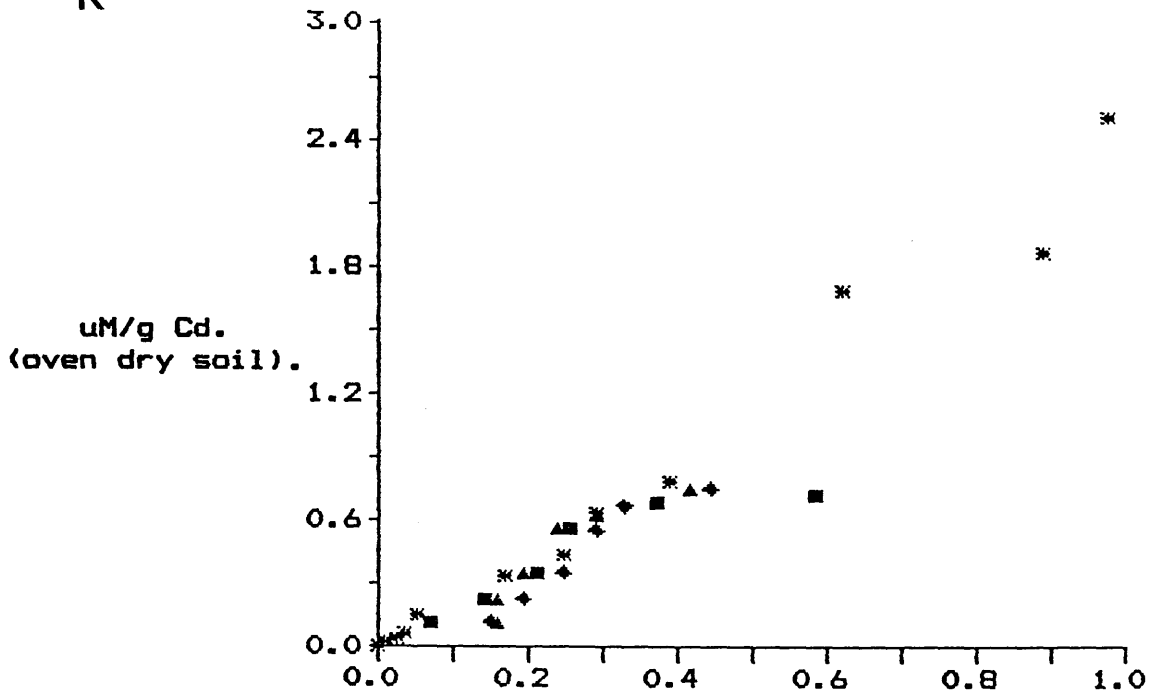
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v ZINC, ARKLESTON HIGH ZINC SOIL.

k



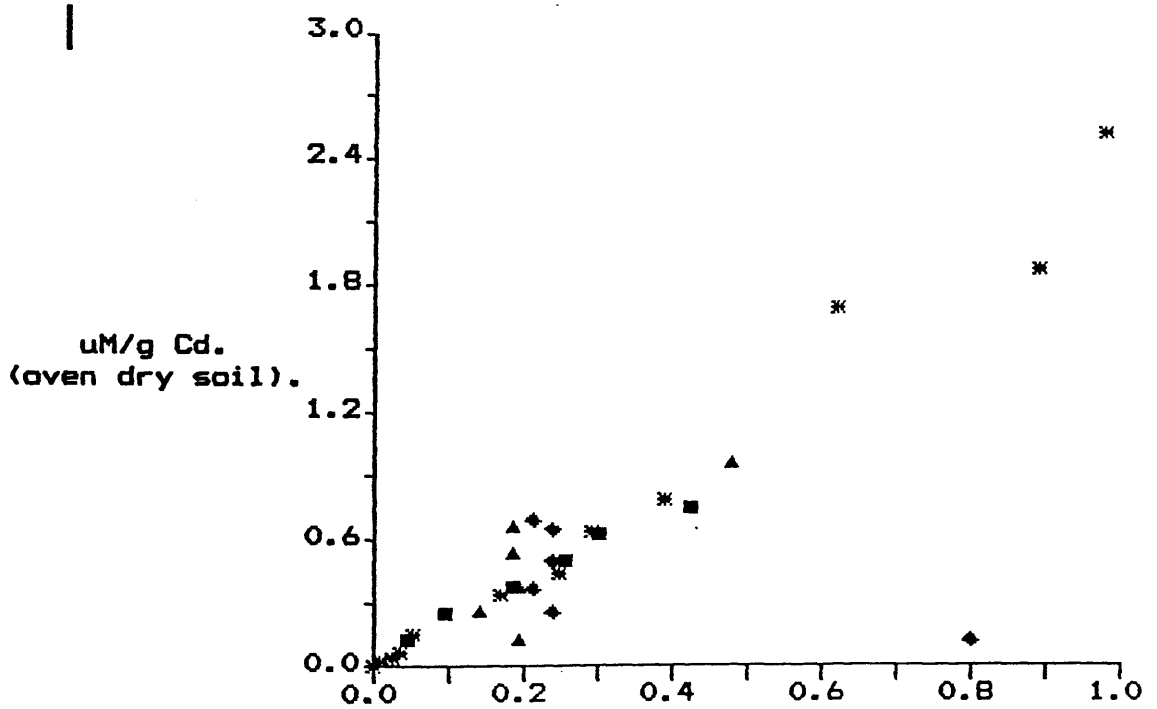
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v POTASSIUM, FEN ARABLE.

l



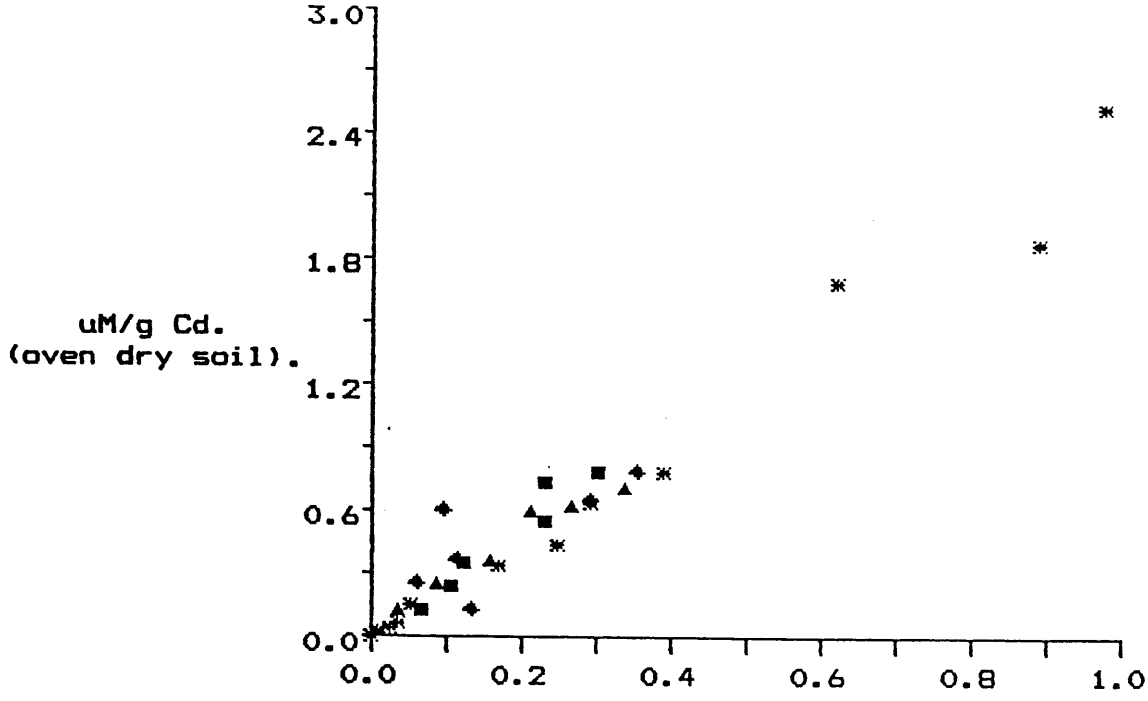
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v IRON, FEN ARABLE.

m



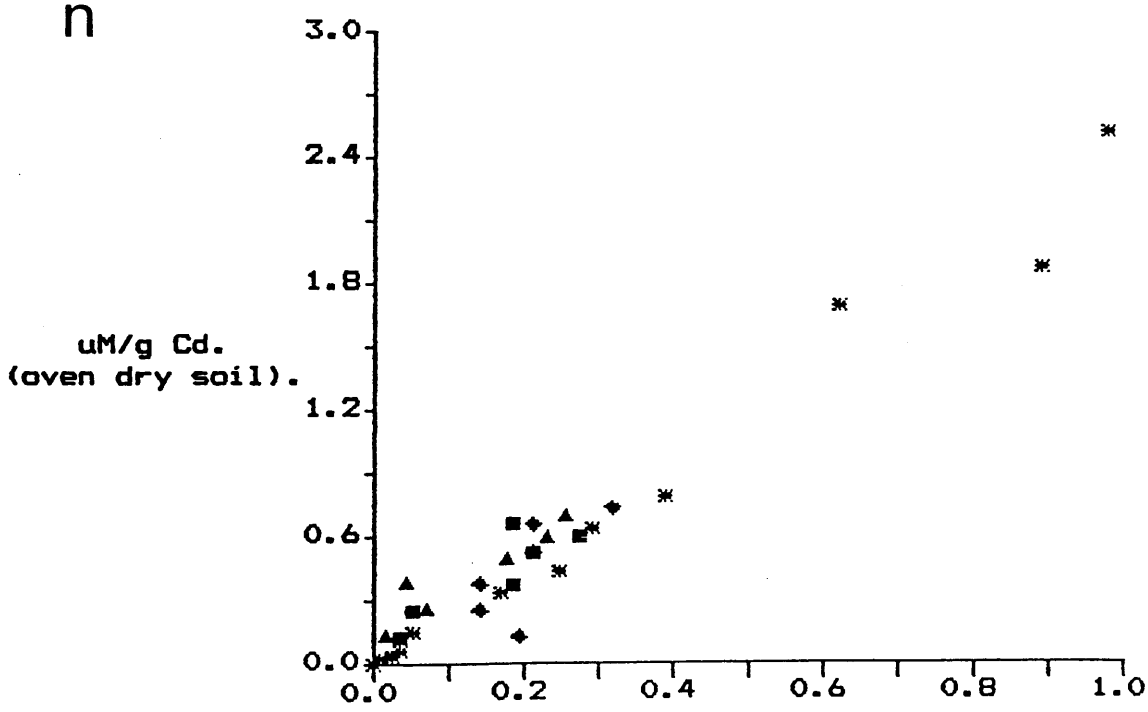
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v COPPER, FEN ARABLE.

n



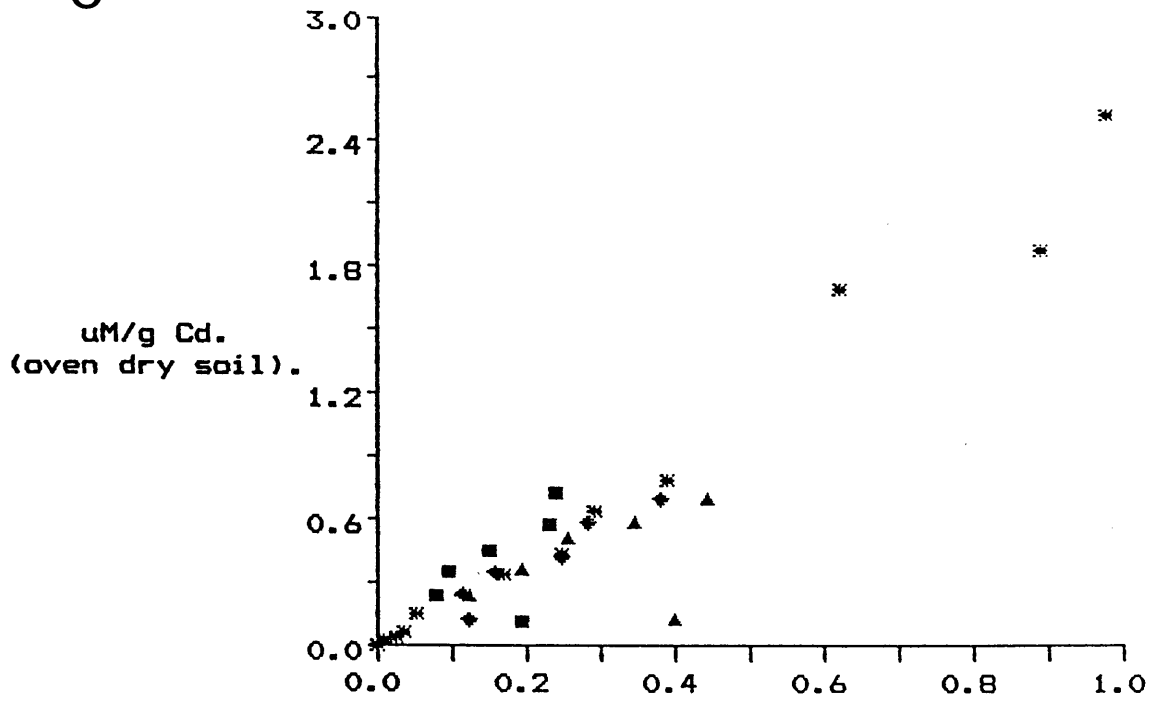
Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v LEAD, FEN ARABLE.

O



Cadmium competition systems in 0.1M NaNO3.

5uM - sq. 15uM - dia. 60uM - tri.

NaNO3 only - *

CADMIUM v ZINC, FEN ARABLE.

(a). K^+ Effect (figure 4.2. a,f and k).

The scatter of points at the higher end of the $NaNO_3$ isotherm for Ark is unfortunate, but, overall, it can be seen that the three levels of K addition had no perceivable influence on Cd removal from solution. This pattern was repeated with the FA soil, whilst in the AHZ soil, there was a slight increase in Cd uptake at all levels of K input, although this follows no clear pattern (ie. there is no correlation between increased Cd sorption and either increasing or decreasing levels of K^+). The levels of addition of K had, it would appear, little impact upon the equilibrium K figures for all the soils (see table 4.3):

Table 4.3. Impact of Added K on Equilibrium values.

Soil	K^+ added/K^+ at equilibrium x 100%.
Arkleston	1.1 - 37.0 %
Arkleston High Zinc	1.1 - 33.0 %
Fen Arable	0.2 - 18.0 %

Certainly, the final K figures in the equilibrium solution are far higher than the additions could account for, indicating that K sorption capacity is being exceeded, so, much as would be predicted, it can be said that K^+ will not, at these levels, compete with Cd for sorption sites. No pH effect was observed.

(b). Fe^{3+} Effect (figure 4.2. b,g and l).

The presence of Fe in the equilibrating solutions, as with K, appeared to have little influence upon the sorption of Cd. Some patterns in Fe relationships with soil could be seen; in all three soils, the equilibrium Fe value at the lowest level of addition was greater than the amount added,

indicating release of iron into solution. At the intermediate addition, the amount of Fe at equilibrium was reduced to the same level as in the lowest addition in both the FA and AHZ soils. The Ark soil demonstrated an increase in its solution-Fe level.

At the highest level of Fe addition, the AHZ soil again reduces the Fe level in solution to that found even at the lowest input; whilst the Arkleston soil, too showed a lower amount of Fe in solution than may have been expected, down to the level of the second addition. Fen Arable, this time, displayed increased Fe in solution. Again, no pH effect could be found.

(c). Cu^{2+} Effect (figure 4.2. c,h and m).

Again, there was no influence of the presence of both Cd and Cu on the pH of the systems, in any of the soils. With the Fen Arable and Arkleston soils, it appears that Cu had no influence upon the uptake of Cd, the experimental points almost directly lying over the $NaNO_3$ lines.

As seen in the potassium figures, there appears to be a slight enhancement of Cd uptake at the lower levels of Cu in the AHZ soil. The 60μM addition brings the points down onto the Na line.

(d). Pb^{2+} Effect (figure 4.2. d, i and n).

The Fen Arable and Arkleston soils showed no great deviation from the NaNO3 line, however, despite the lack of any major pH trend in the Arkleston soil, the Fen Arable was marginally, but consistently, higher than in other systems.

Regarding the AHZ soil, there is the beginning of a competitive trend: the two lower levels follow (with a slight increase upon) the $NaNO_3$ line, whilst at the 60μM level of competing ion, the uptake points were shifted downwards, suggesting a degree of selectivity for Pb over

Cd. Again there was no pH trend.

(e). Zn^{2+} Effect (figure 4.2. e, j and o).

None of the three soils showed any influence of Zn upon the removal of Cd from solution; indeed, for the two Arkleston soils, the data points followed the non-competitive isotherm almost exactly. The points in the Fen soil were rather scattered, but followed the general trend of the $NaNO_3$ graph. The influence of the combination of the two heavy metals on the solution pH was inconsequential.

In the Arkleston soil, there was a fair degree of point scatter, but there appeared to be little depressing influence of the combination of cations on Cd removal from solution: even at the higher levels, the 100, 200 and 300μM levels, the data points still follow those obtained in $NaNO_3$ alone.

The AHZ soil demonstrated this lack of influence using the mixture of competing cations. The presence of Cu alone has the somewhat curious effect of beginning to reduce the retention of Cd until ≈ 12.0μM (equilibrium) Cd, when the sorption curve moves sharply upwards.

Fen Arable soil had no remarkable features with regard to the influence of Cu or the mixture of cations on Cd sorption from solution.

Copper

(the relevant graphs are shown in figures 4.3. a-f)

(a). Fe^{3+} Effect.

The Arkleston soil showed almost no change from the $NaNO_3$ line when Fe was introduced into the system, except at the higher levels, where the isotherm took a sharp turn upwards. With the AHZ soil, the Na line curved above the Fe line, showing quite a marked reduction in Cu uptake, whilst the FA soil demonstrates that for a given level of Cu input, the presence of Fe in solution actually improved the level of

removal, over Na.

In all three soils, there appeared to be a general lowering of pH in all the Cu-Fe systems, especially so at the higher levels of additions.

(b). Cd^{2+} Effect.

The Ark soil displayed no pH change at the low levels, the 100, 200 and 300μM additions did bring about quite a reduction in pH; this aside, Cd at all levels in this soil reduced the amount of Cu taken up from solution. Much the same can be said of the other two soils.

(c). Pb^{2+} Effect.

The highest amounts of Cu were taken up by the Arkleston soil in the systems containing Fe, Na and also from the Pb system, with no observable influence on the pH of the systems: again, this pattern was repeated in the other two soils.

(d). Zn^{2+} Effect.

In the two Arkleston soils, the presence of Zn had a middling influence on the sorption isotherms, below Fe, Na and Pb, but above Cd and the mixture of cations. In the Fen soil, the Zn isotherm overlay the mixture line, but was still higher than the Na and Cd lines.

(e). $Fe^{3+} + Cd^{2+} + Pb^{2+} + Zn^{2+}$ Effect.

In all three soils there was a depressing influence of equimolar amounts of these ions on the solution pH, more so than in any of the other systems. In the two Arkleston soils, it has the second most diminishing effect on Cu retention. The Fen soil shows that Cu uptake is the same in the Zn only system, and higher than the Na and Cd isotherms.

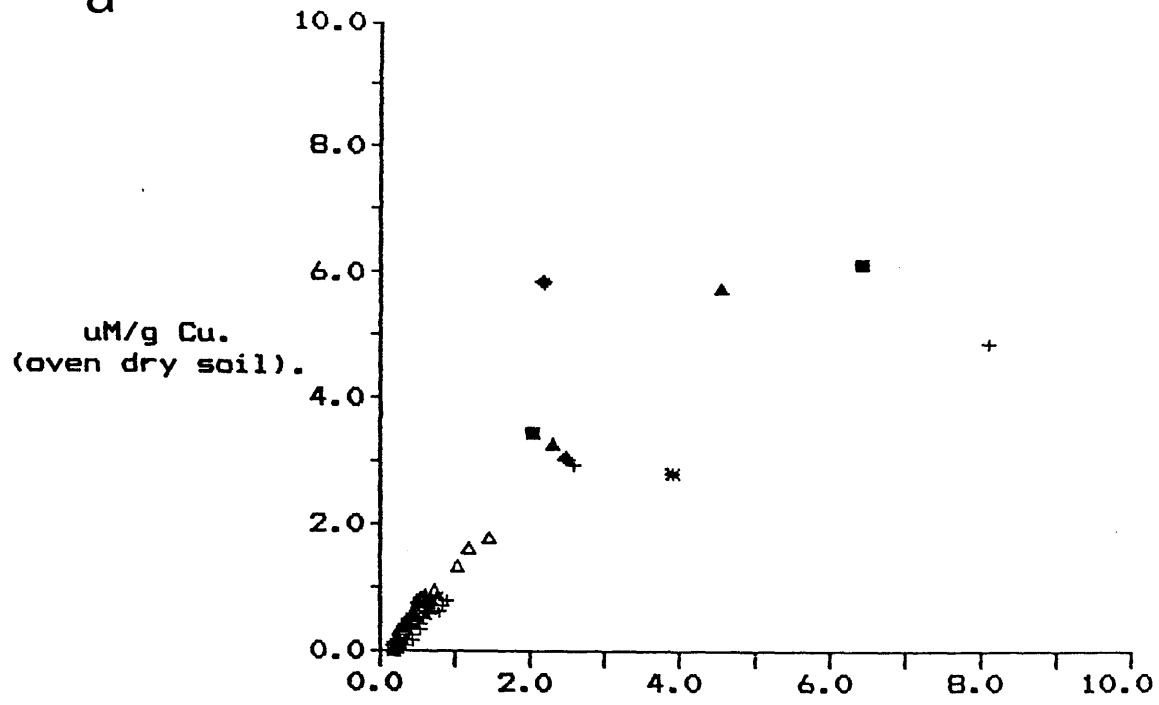
Figure 4.3. Cu Competitive Isotherms.

Figure 4.3. Cu Competetive Isotherms

(a). Ark-full range (c). AHZ-full range (e). FA-full range

(b). Ark-lower end (d). AHZ-lower end (f). FA-lower end

a



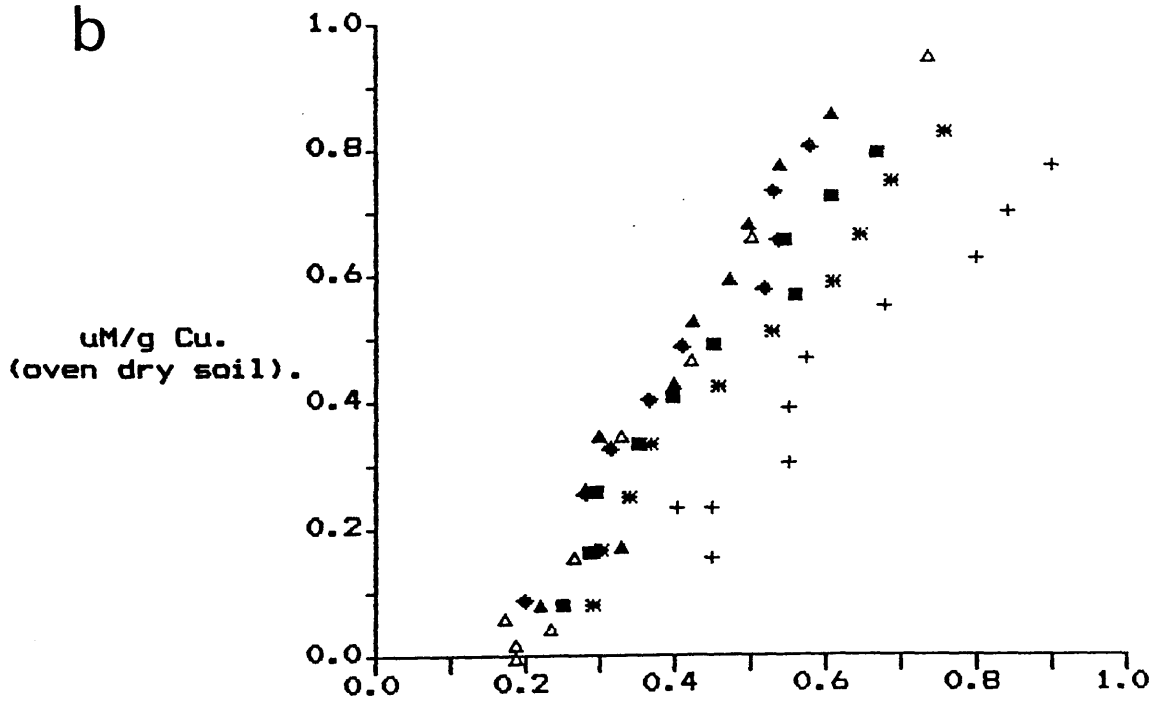
Copper competition systems in 0.1M NaNO3.

All - * Zn - sq. Pb - tri. Fe - dia.

Cd - + NaNO3 only - open tri.

ARKLESTON.

b



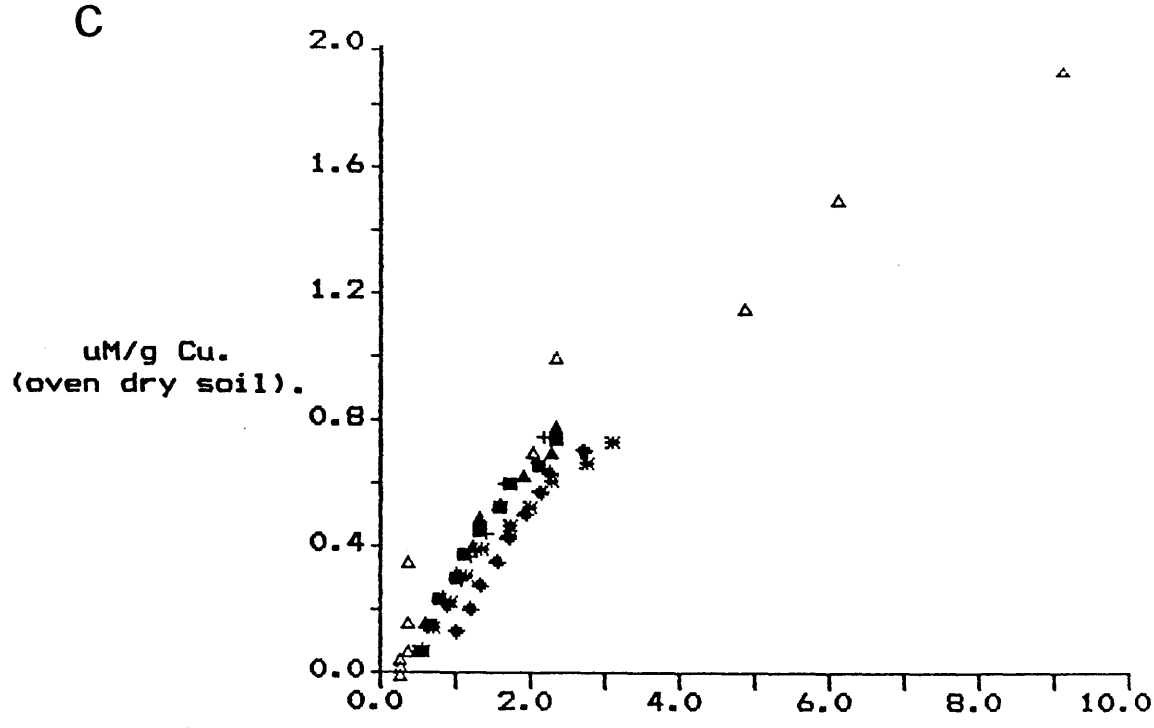
Copper competition systems in 0.1M NaNO3.

All - * Zn - sq. Pb - tri. Fe - dia.

Cd - + NaNO3 only - open tri.

ARKLESTON.

c



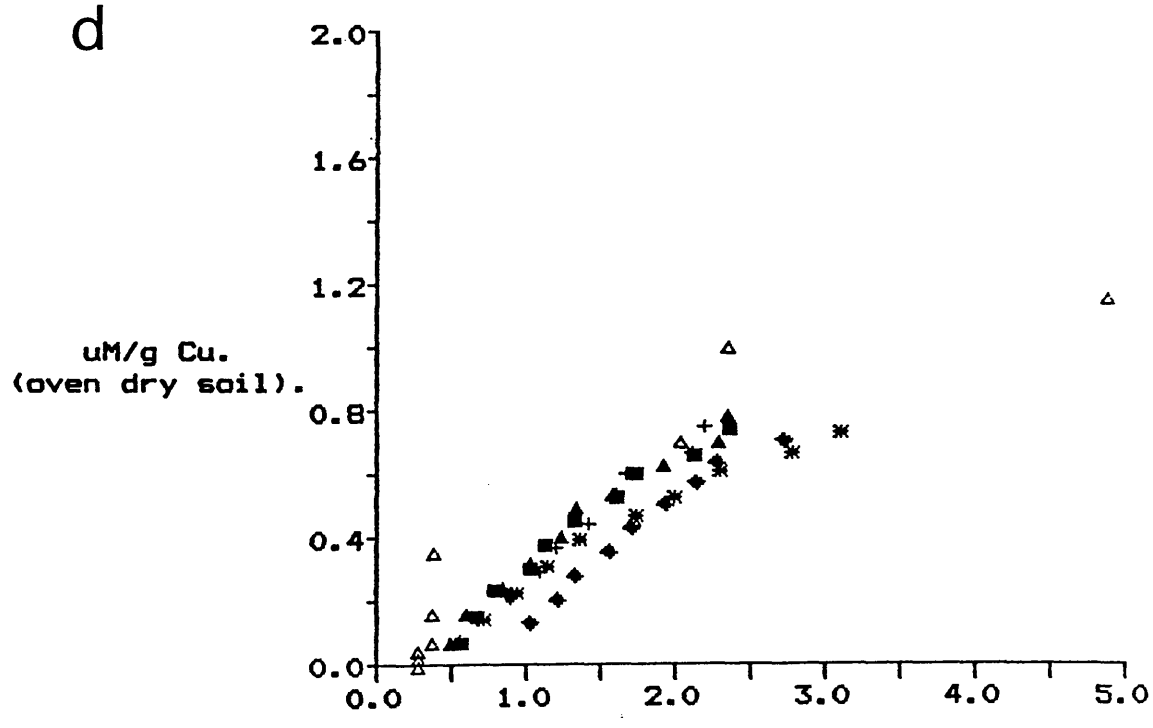
Copper competition systems in 0.1M NaNO3.

All - * Zn - sq. Pb - tri. Fe - dia.

Cd - + NaNO3 only - open tri.

ARKLESTON HIGH ZINC.

d



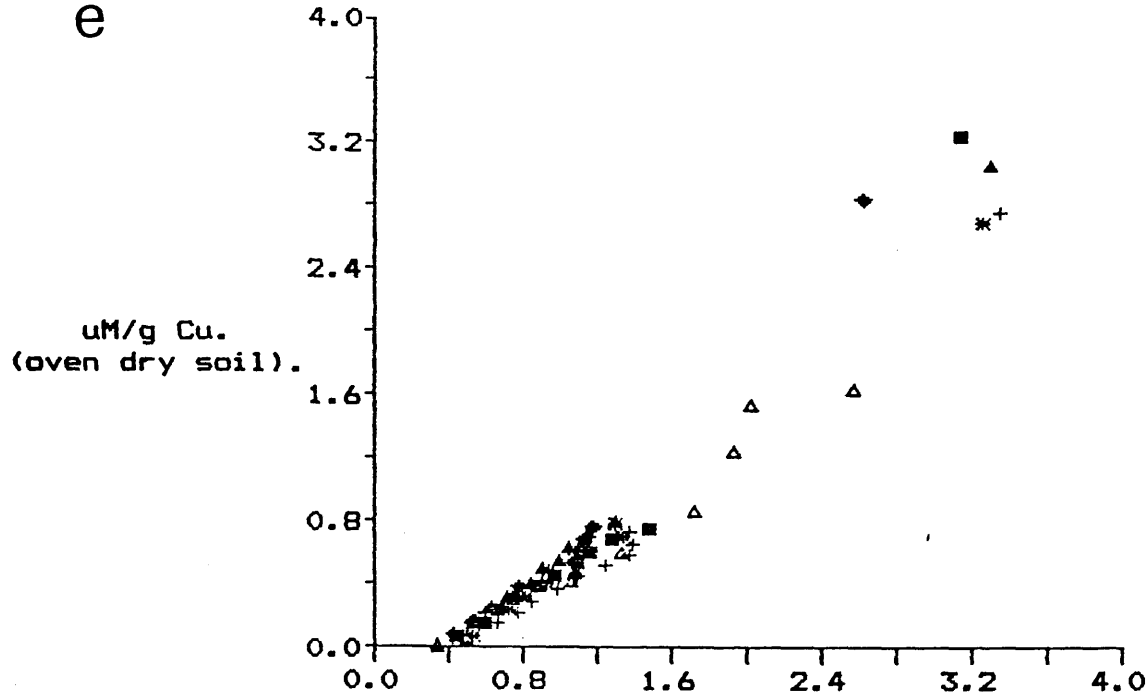
Copper competition systems in 0.1M NaNO3.

All - * Zn - sq. Pb - tri. Fe - dia.

Cd - + NaNO3 only - open tri.

ARKLESTON HIGH ZINC.

e



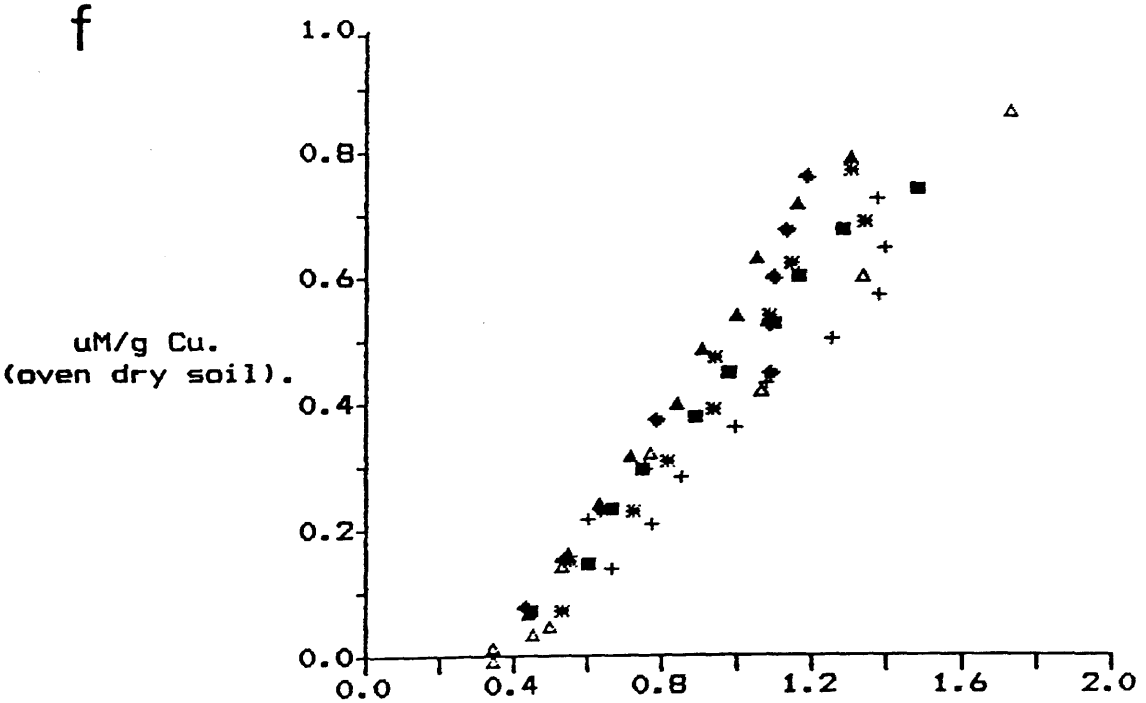
Copper competition systems in 0.1M NaNO3.

All - * Zn - sq. Pb - tri. Fe - dia.

Cd - + NaNO3 only - open tri.

FEN ARABLE.

f



Copper competition systems in 0.1M NaNO3.

All - * Zn - sq. Pb - tri. Fe - dia.

Cd - + NaNO3 only - open tri.

FEN ARABLE.

4.3.2. Discussion.

In the previous chapter, the discussion on the use of the Langmuir equation in a mechanistic sense put forward the notion that the levels of Cd and Cu used in the sorption experiments would, intuitively, lie below the site saturation level, and, hence, if the Langmuir theory could also be applied to as heterogeneous a material as soil, it should have resulted in straight line descriptions for both Cd and Cu sorption. This was clearly not the case, so is it possible that the available sites for metal uptake were reaching saturation, or that discrete groups of sites were involved in the removal process? The findings of this series of experiments demonstrate one very broad trend - that at the levels of metals employed in both approaches to this investigation, uptake of Cd or Cu could be said to be independent of the presence of other metals, one of which, iron, has a higher charge density than Cd or Cu, and others which are considered to be behavioral analogues for these two metals - Zn and Pb respectively.

In a paper on the changes in availability of Cu in soil with time, Miller *et al* (1987) used Pb ions to specifically desorb Cu (the affinity of Cu for organic molecules is well documented; Xian (1989) has shown that Pb resides mainly in the organic fraction of soils, whilst Wild *et al* (1987) noted that when plants were grown in flowing nutrient cultures, Pb remained strongly bound in the plant roots. Adam *et al* (1989) have shown that increasing the inputs of Pb to soil had no influence on plant uptake, implying that it assumes a very plant-unavailable (immobile?) form in soil), whilst Brown *et al* (1983) intimated that Zn and Cd should behave similarly in soils. The latter prospect, from a chemical point of view, may be regarded as quite

acceptable, given that Cd and Zn occupy the same group of the periodic table and that Cd is usually found in the Zn minerals.

In chemical terms, there seems to be little reason why Pb should compete on the same grounds as Cu for uptake: Cu is classed as a borderline acid (according to HSAB principles) whilst Pb is definitely soft. They do not occupy the same group in the periodic classification, and Pb favours (II) and (IV) oxidation states (Cu - (I) and (II)). A further reason militating against the idea of Cu-Pb competition might be found from considering their ionic radii;

Cu(II) 0.071-0.087 nm

Pb(II) 0.121-0.144 nm

Pb(II) will thus have a lower charge density than Cu(II) and probably a smaller hydrated radius. Whilst Cu(II) will form inner-sphere complexes, which due to the ability of Cu(II) to polarize electrons, show a degree of covalency. Pb(II) bonds will be outer-sphere and weakly ionic. Observations in the literature appear to run contrary to all of this - Elliott *et al* (1986) suggested that Pb is 'selected' over Cu, as did Kinniburgh *et al* (1976): what they failed to consider, though, is the independent removal of metals from solution to specific 'batches' of sites - this point will be further discussed.

Zinc showed no evidence of displacing Cd, and it can be presumed that uptake of both elements could be considered to be additive, ending up in different but specific sites. Given the similarity of the data points to the specific ($NaNO_3$) line, it would seem safe to state that even in the presence of Zn, Cd still ended up on the same sites: Similarly in the presence of Pb, K, Fe and Cu. Only in the

presence of all the cations (equimolar Pb + Cu + Zn + Fe) did there appear to be a depressing influence, and this only in the AHZ soil.

No influence was expected from K, and indeed, none was shown, the soils releasing quite considerable amounts of K, any additions having little impression on the native soil levels. In the AHZ soil there was a slight increase in the sorbed Cd figures, relative to the Na^+ ones: in light of the fact that the amount of K added to each batch little altered the non-amended equilibrium figures, this can probably be ascribed to experimental error and/or the variability of the soil itself. Garcia-Miragaya and Page (1976) have shown a slight degree of Cd-K interaction in experiments on Na, K, Ca and Al saturated Montmorillonite, where Cd uptake on to the clay surface was hindered by K relative to Na.

The presence of Fe in the systems raises the possibility, not just of competition, but of precipitation of a mixed material - Pulford (1986) and Brummer *et al* (1983) have suggested that such materials may limit Zn solubility in soils, whilst Lindsay (1979) gives a stability constant for the copper-iron mixed oxide, $CuFe_2O_4$; no such material has been proposed for Cd, but given the heterogeneity of soils, it is possible that a non-regular solid phase could form. A further possibility is the formation of a hydrous Fe-oxide, providing a highly active surface for retention. Thus we have a situation where the presence of another ion yields the potential for either diminished or increased sorption, depending upon its reaction. With all three soils in the Cd experiments, at the lowest level of Fe input, there was an increase in the amount of Fe in solution: obviously, at this level, it was below the saturation level of the most labile form of Fe in the soil - this situation is overcome at the two higher levels: There is a general trend of constant Fe

concentration, implying a solubility control of Fe (it may also be some form of 'sink' for excess Fe, controlled by an overall equilibrium constant). The FA soil showed an increase in solution Fe at the higher level.

At the lower levels, where Fe was being released into solution, and as there was an almost constant level of solution Fe, it cuold be concluded that there was no element of direct competition between Cd and Fe, as any excess Fe in solution was taken up by some soil reservoir, although it is possible that this sink was denying uptake sites to Cd. Even at the 60 μM addition of Fe, there is no significant pH decline which would provide evidence of hydroxide formation, but the Fen Arable soil began to show quite a degree of point scatter at the 15 and 60 μM levels of Fe, possibly due to the onset of a heterogeneous precipitate or solid-phase.

The Arkleston High Zinc soil presents an intriguing picture in relation to Zn competition. The other two soils showed typical sorption isotherm characteristics, and all three showed that Zn cannot compete with Cd for uptake, even when present at twice the concentration of the Cd. Christensen (1987 a & b) has based some of his work on the Cd-Zn interaction in soils, and whilst he did find that zinc could inhibit Cd sorption, the levels of Zn were much greater than those of Cd (admittedly still falling within the realms of soil amended by a sludge material). Analogous to the iron systems, there appears to be a Zn reservoir in the soil, which, at the lower levels, maintains a constant solution level of Zn: solution levels, even at 80 μM equilibrium level still appear to be somewhat below the soil saturation level. These results seem to stand in contrast to statements of similar types of behaviour of Cd

and Zn in soils.

The lead and copper competitive systems, again, showed no influence in the removal of Cd by surfaces, and unlike K, Fe and Zn, all soils take up Pb and Cu in typical isotherm patterns.

At the higher levels of addition in all cases, a relative order of uptake can be deduced:

Arkleston: Cu > Cd Pb > Zn > Fe > K

Arkleston High Zinc: Cu > Fe ≥ Pb > Cd >Zn > K

Fen Arable: Zn > Cd > Cu > Pb > Fe > K

Again, as in the sorption isotherms of the previous chapter, the pattern of the more acid soils taking up more Cu than Cd is maintained, whilst the more calcareous, high pH Fen soil reverses this trend. The Arkleston High Zinc soil is known to possess a high level of Zn, and, not surprisingly, this element features in the low position in the selective sequence, preceded by Cd, which would tend to confirm that these two metals are akin to one another, in this instance, and in the Fen soil, where the two appear at the head of the list.

Looking at the situation from the point of view of a given ion's influence upon the levels of a second ion in solution, one might compare the systems, at a given level, in terms of the $[Cd^{2+}]_{solution}$: $[Cd^{2+}]_{sorbed}$ ratio. Thus, an ion which competes well with Cd will tend to make this ratio increase (this is the inverse idea of the selectivity coefficient, K_d which is used as a measure of a soils affinity for a solution component (Sposito, 1984), rather, this approach looks at the selective ability of the solution), whilst one which competes to a lesser extent will tend to give a lower ratio. With these considerations in mind, and bearing in mind too that the visual representations of these systems implied

minimal competition, then with this more mathematical/quantitative construct of the situation, differences can be seen in the behaviour of the Cd systems at the 15μM addition level;

Arkleston: $Zn > Cu \geq K > Pb > Fe$ (Ratio S = 14 %)

Arkleston High Zinc: $Zn > Cu > Fe > Pb > K$ (Ratio S = 5 %)

Fen Arable: $K > Fe > Zn > Pb > Cu$ (Ratio S = 33 %)

The S (Relative Error) values reflect the variation in the ratio values relative to the mean, and the implication is that the higher this value is, the more "real" any variation in the ratio is.

The curiosity thrown up by this view of the data is that K appears to be competing with Cd in the Arkleston and Fen Arable systems. This phenomenon may be a function of the soils having a very high sorption capacity for, in the former, Pb and Fe, and in the latter, Fe, Zn, Pb and Cu, removing, independently, most of the added competing ion, regardless of the Cd sorption.

Whilst Cu may not be influencing Cd uptake to any great degree, this does not rule out the possibility of Cd competing with Cu (or any of the other elements studied above). The view given by the Cu competition results reflects those of the Cd systems ie. at the levels of competing ions studied, there is no competitive effect, even at the very, comparatively, high levels of Cu examined. In the Fen Arable soil, where, in view of its high pH, it would be predicted that the introduction of Fe into the system brings about precipitation of an oxide form, particularly at the high levels of addition; there is slight evidence for this in the way in the upward trend for Cu uptake. This pattern is somewhat surprisingly repeated in the Arkleston soil, whilst the isotherms for the other systems appear to be following a projection of the $NaNO_3$ line. Certainly, in all

three soils, the addition of Fe, in the mixed systems too, seems to lower the supernatant pH, relative to that in the mono-ion systems (Chapter 3). This may point towards precipitation were it simply due to Fe^{3+} - H^+ exchange, it would be difficult to account for the fact that the Cu sorption is not greatly reduced due to proton competition relative to the $NaNO_3$ systems.

Placing several ions in competition with one another for uptake moderates the effect of the reduction in the number of available sites and the drop in pH by forming new (Fe-oxide?) surfaces onto which ions may be sorbed: This could explain the fact that the presence of a single divalent competitive ion (Cd^{2+}) could lower the soils uptake of Cu to a greater extent than the combination of Cd + Fe + Pb + Zn. In the Arkleston High Zinc soil, the paucity of specific Cu sites showed itself when any other ion was introduced, and we can construct the following sequence of effectiveness for competing ions, based on a visual appraisal of the sorption graphs;

Arkleston: Cd > All > Zn > Pb = Fe

Arkleston high Zinc: Cd > All > Pb = Zn = Fe

Fen Arable: Cd > All = Zn > Pb = Fe

However, if we judge competitive ability, as in the Cd discussion, on the ability of an ion to increase the concentration of another in solution, then the following sequences are arrived at:

Arkleston: Cd > All > Zn > Pb ≈ Fe (S = 12 %)

Arkleston high Zinc: Cd > All > Fe > Pb > Zn (S = 16 %)

Fen Arable: Cd > All ≈ Zn > Pb ≈ Fe (S = 11 %)

(figures calculated at the 15μM addition level).

In view of the data, Pb and Fe turn out to be the poorest competitors with Cu and, not surprisingly, given the native

high presence of Zn, the Arkleston high Zinc soil shows that Zn is a poor Cu competitor, as all the specific sites are saturated with Zn and Cu.

It may be too strong to dismiss the idea of certain metals showing similar behavioural characteristics in soils, such as Pb and Cu, and Zn and Cd. The above set of experiments show that the Cu homologue Pb is a poor competitor for Cu sites. In contrast, the solution:sorbed ratio in the Cd experiments was most influenced by the presence of Zn. However, the two findings are not irreconcilable, they merely represent the difference in site availability in each soil, with respect to either Cu or Cd or the other ions used. The following example should make this more clear:

If a soil has 40 sites for uptake, 10 specific to Cu and 10 specific for Pb, and 20 of variable Cu - Pb affinity, at equimolar inputs up to the amount required for saturation of the 20 Cu and Pb sites, uptake of one will be unaffected by the other: no competitive effect will be noticed. When this allocation has been utilized, one can envisage a molecular "scrum" for the remaining sites, and a depressing effect will be seen in the uptake of one ion relative to the other. Where the number of sites is less balanced, say 15 for Zn, 5 for Cd and 20 indeterminate, the effect will become visible at lower concentrations.

This description applies insofar as the comparison of two ions is concerned, the picture becomes less clear when a series of competitions is considered.

4.3.3. Anion and Concentration Effects.

The data tables for this section are included in appendix 4.

The graphs representing the influences of chloride, sulphate and citrate on Cd and Cu sorption, relative to nitrate, are shown in figures 4.4 (a-d) and 4.5. (a-d) respectively. From these, and considering the data in the appendix, the anion effects, in terms of decreasing sorption,can be summarized thus;

Cadmium:

Arkleston;	$NO_3^- \approx SO_4^{2-} > Cl^- >>$ Citrate
Arkleston High Zinc;	$NO_3^- \approx SO_4^{2-} > Cl^- >>$ Citrate
Fen Arable;	$NO_3^- > SO_4^{2-} > Cl^- >>$ Citrate

Copper:

Arkleston;	$Cl^- > NO_3^- > SO_4^{2-} >>$ Citrate
Arkleston High Zinc;	$NO_3^- > Cl^- > SO_4^{2-} >>$ Citrate
Fen Arable;	$Cl^- > NO_3^- > SO_4^{2-} >>$ Citrate

And for both sets of data, the following pH sequences apply;

Arkleston;	Citrate $> SO_4^{2-} \approx Cl^- > NO_3^-$
Arkleston High Zinc;	Citrate $> SO_4^{2-} > Cl^- > NO_3^-$
Fen Arable;	Citrate $> SO_4^{2-} > Cl^- > NO_3^-$

Despite the fact that the citrate systems started out, and finished up as high pH systems (>pH7), in all instances, the presence of this organic anion managed to reduce both Cd and Cu uptake, indeed, in some instances it showed the potential to be an extractant. This clearly demonstrates the inter-active role played by pH and soluble organic

material in solution chemistry.

Figure 4.4. Influence of Anion on Cd Sorption, I=0.1.

Figure 4.4.

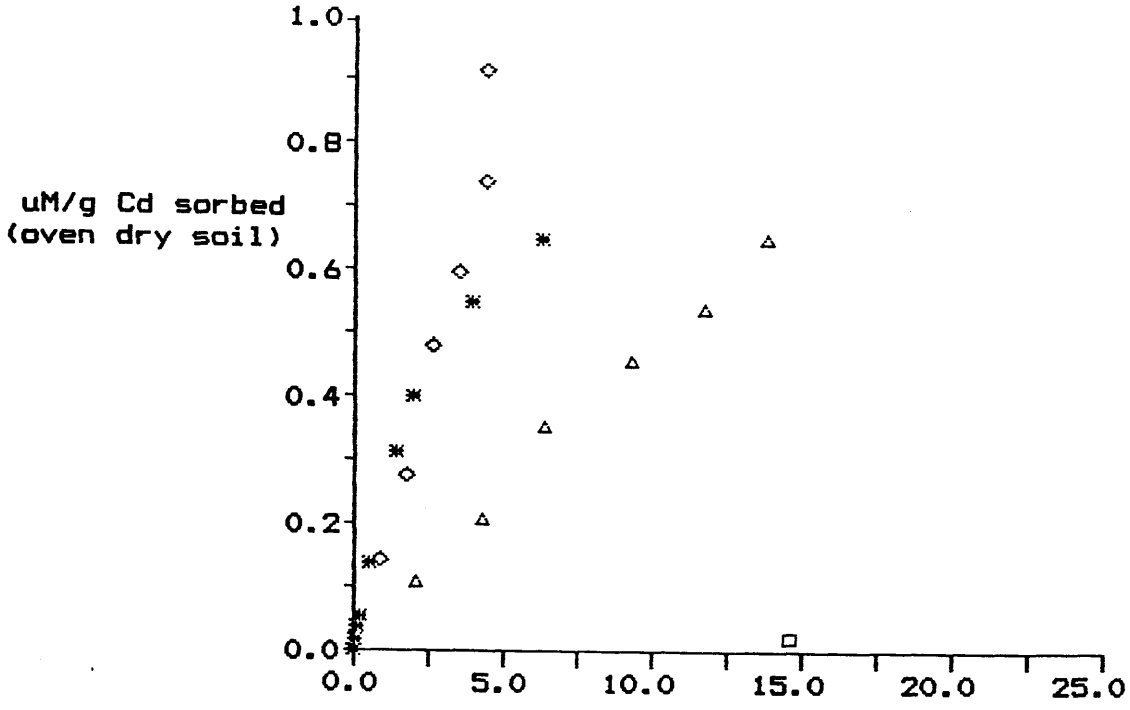
(a). Ark - NO_3^-, Cl^-, and SO_4^{2-}.

(b). AHZ - NO_3^-, Cl^-, and SO_4^{2-}.

(c). FA - NO_3^-, Cl^-, and SO_4^{2-}.

(d). Citrate - Ark, AHZ and FA.

a

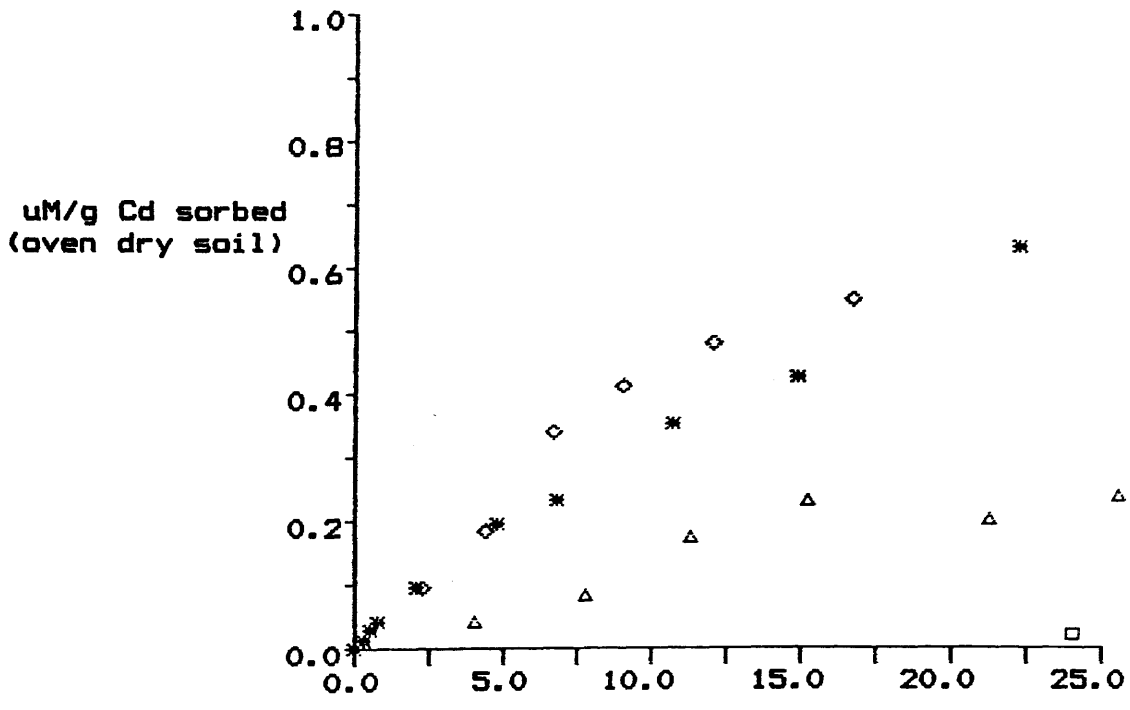


Influence of anion on Cd sorption.

NO3 - * SO4 - dia. Cl - tri. Cit. - sq.

ARKLESTON SOIL.

b

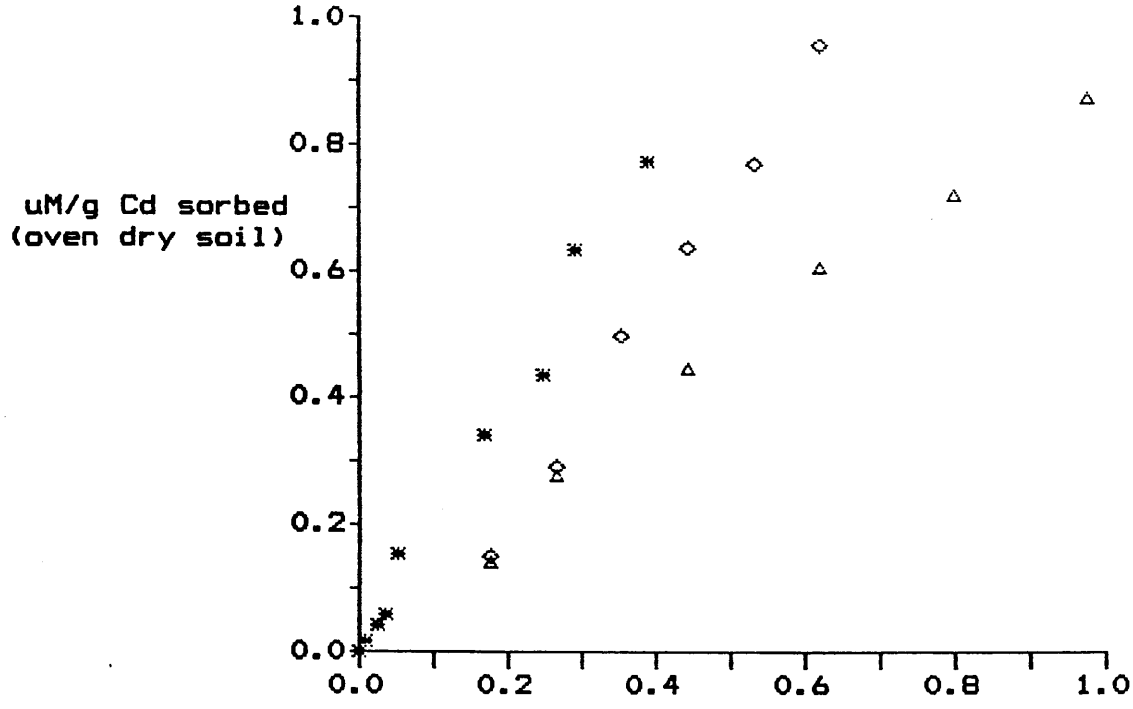


Influence of anion on Cd sorption.

NO3 - * SO4 - dia. Cl - tri. Cit. - sq.

ARKLESTON HIGH ZINC SOIL.

c



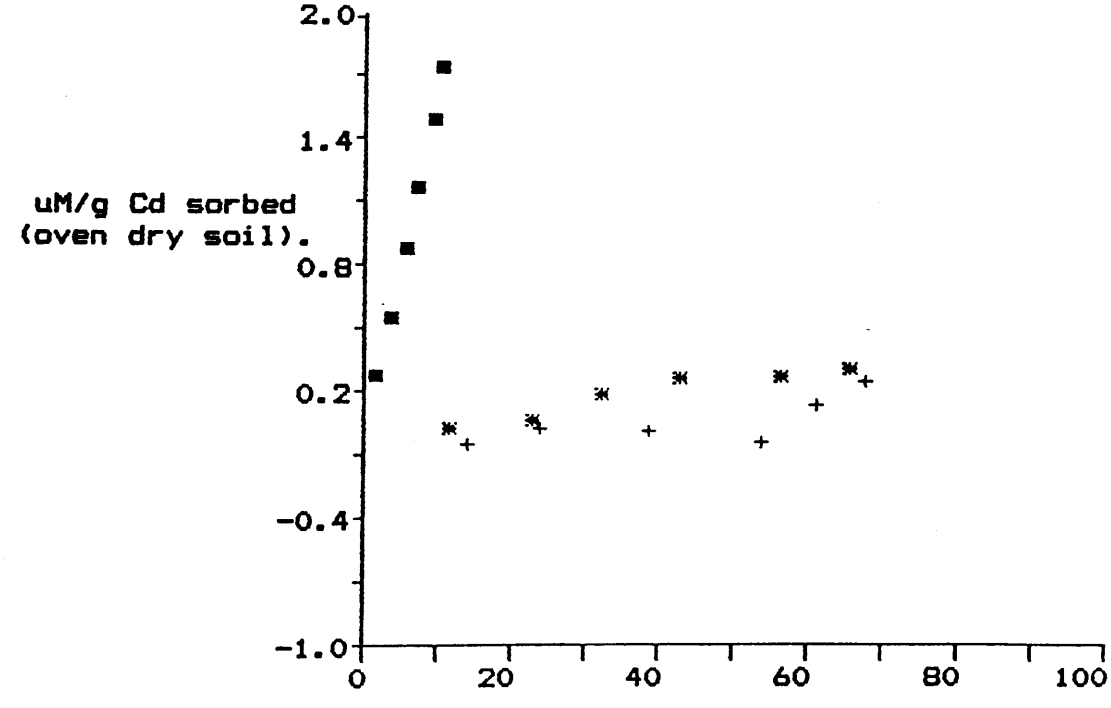
uM Cadmium at equilibrium.

Influence of anion on Cd sorption.

NO3 - * SO4 - dia. Cl - tri. Cit. - sq.

FEN ARABLE SOIL.

d



uM Cd at equilibrium.

Influence of Citrate on Cd sorption.

ARK - * AHZ - + FA - sq.

Figure 4.5. Influence of Anion on Cu Sorption, I=0.1.

Figure 4.5.

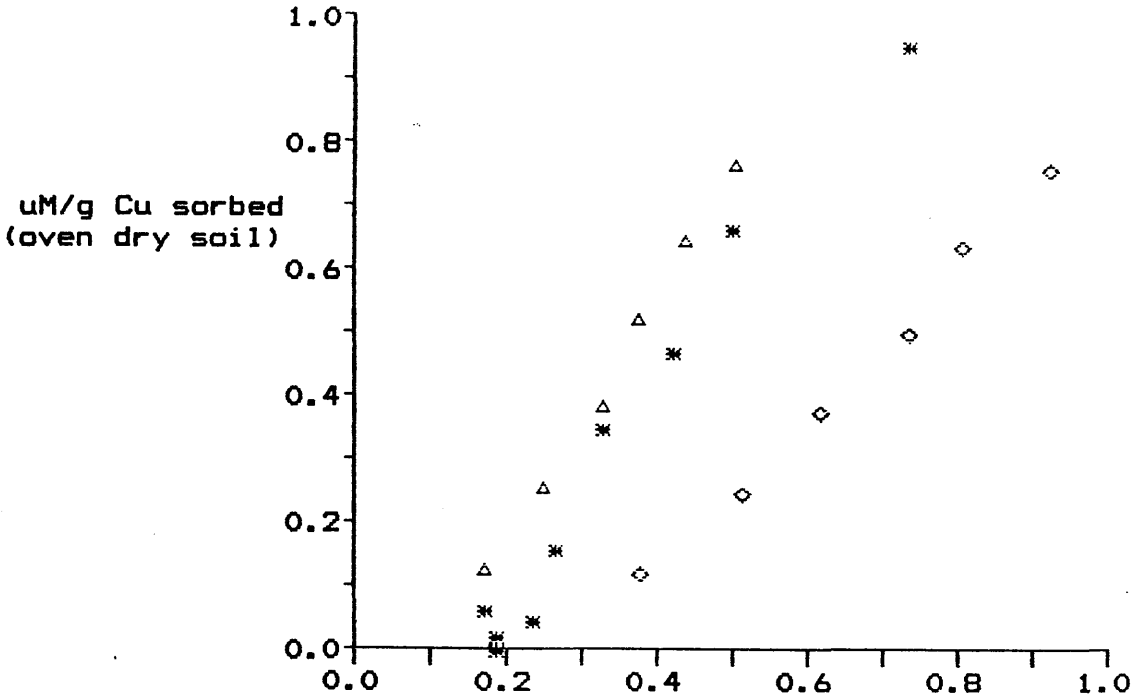
(a). Ark - NO_3^-, Cl^-, and SO_4^{2-}.

(b). AHZ - NO_3^-, Cl^-, and SO_4^{2-}.

(c). FA - NO_3^-, Cl^-, and SO_4^{2-}.

(d). Citrate - Ark, AHZ and FA.

a

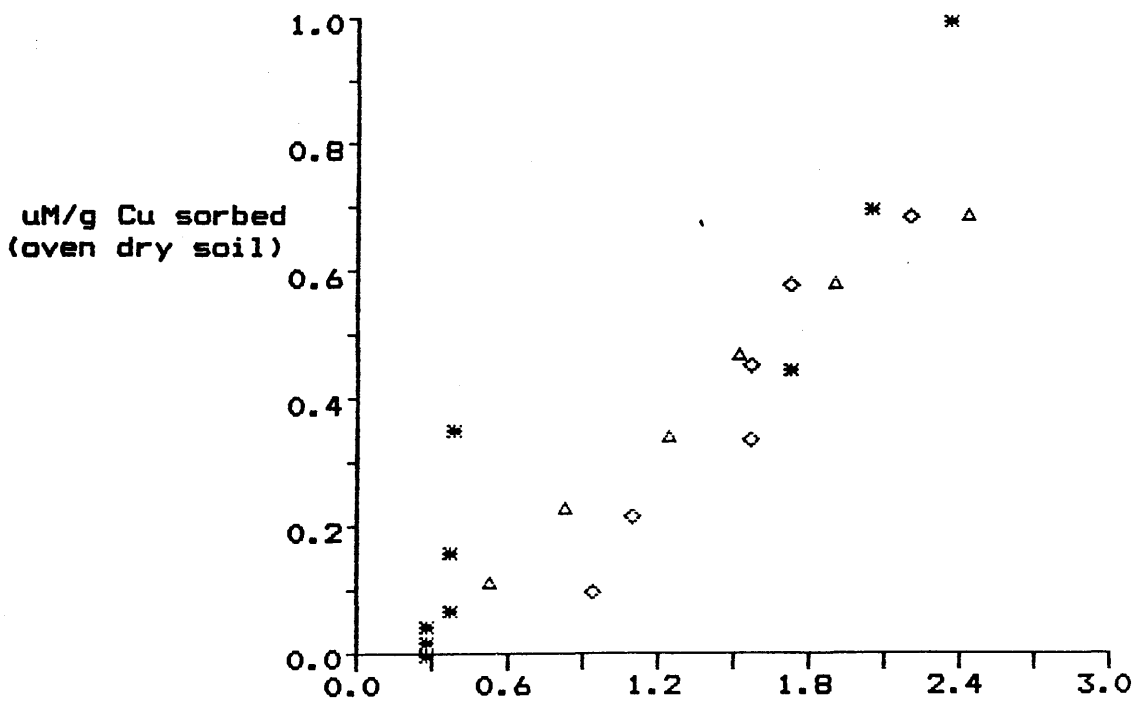


Influence of anion on Cu sorption.

NO3 - * SO4 - dia. Cl - tri.

ARKLESTON SOIL.

b

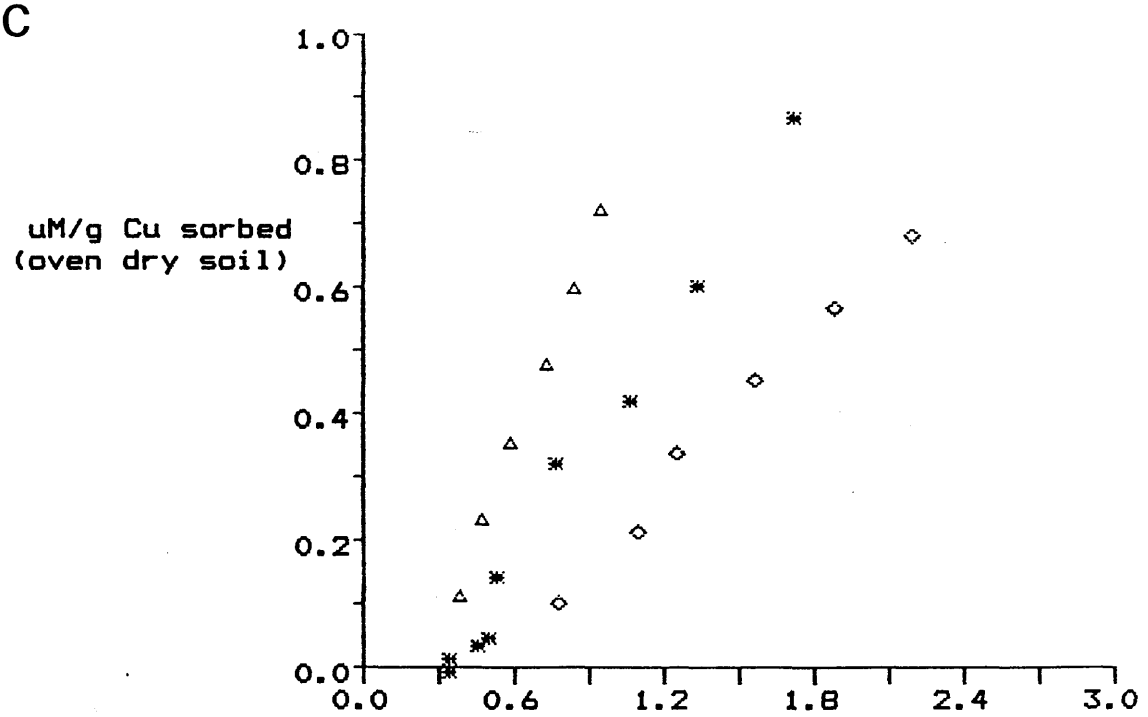


Influence of anion on Cu sorption.

NO3 - * SO4 - dia. Cl - tri.

ARKLESTON HIGH ZINC SOIL.

c

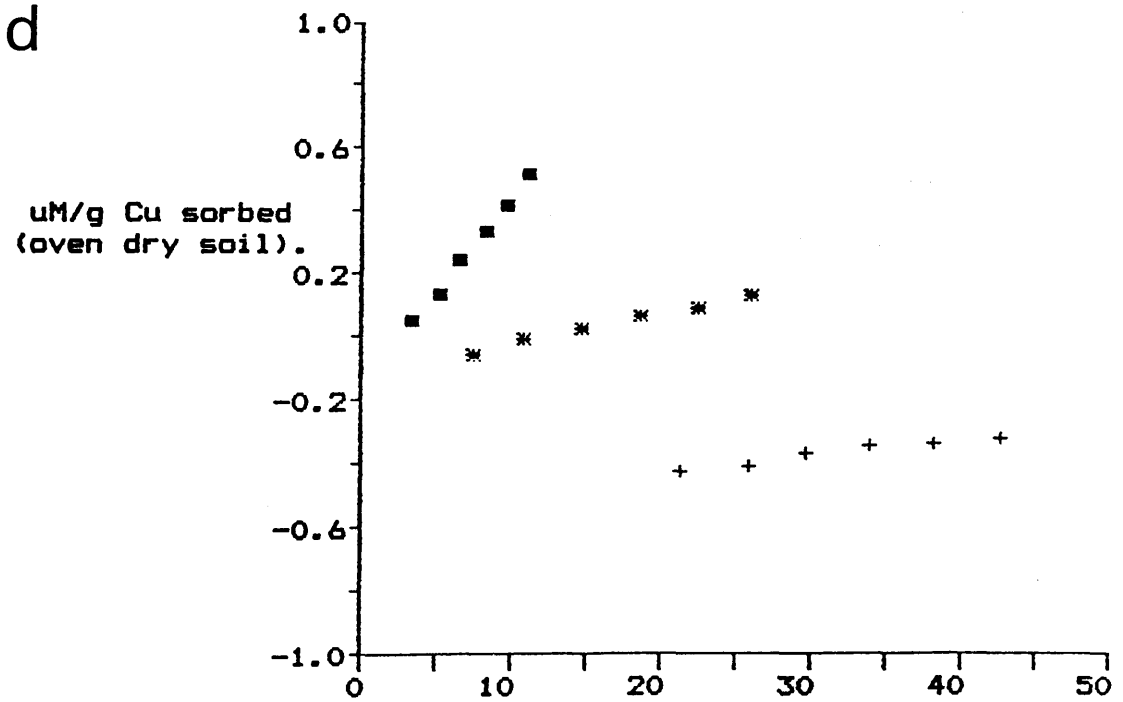


Influence of anion on Cu sorption.

NO3 - * SO4 - dia. Cl - tri.

FEN ARABLE SOIL.

d



Influence of Citrate on Cu sorption.

ARK - * AHZ - + FA - sq.

If the Cd graphs are examined more closely, at equilibrium concentrations greater than 5 μM, in the Arkleston soil, uptake from SO_4^{2-} begins to exceed that from NO_3^-; a similar event is seen in the Arkleston High Zinc system. Below 0.2 μM, in the Fen Arable soil, the uptake of Cd becomes independent of SO_4^{2-} and Cl^-, and the two sets of data converge. The similarity of the SO_4^{2-} and the NO_3^- curves could be evidence for the uptake of ($Cd(SO_4)^0$) and ($Cd(NO_3)_2^0$).

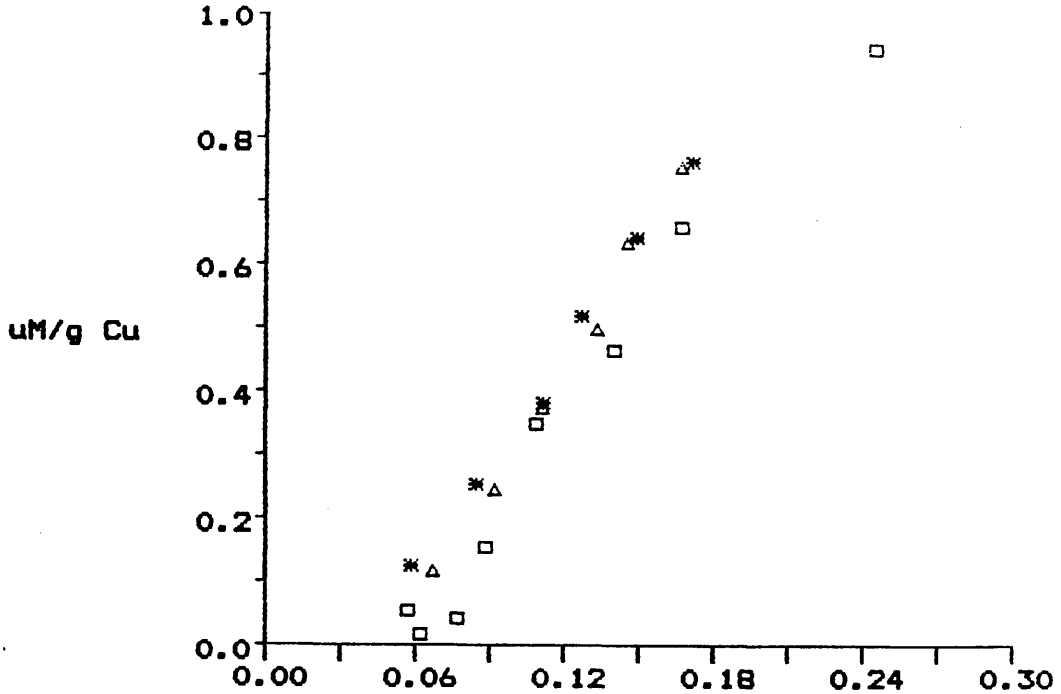
In the Cu systems, where citrate shows that it can extract Cu, no continuous level of Cu is maintained in solution, thus negating the idea of solubility considerations being responsible for controlling the solution levels of metals.

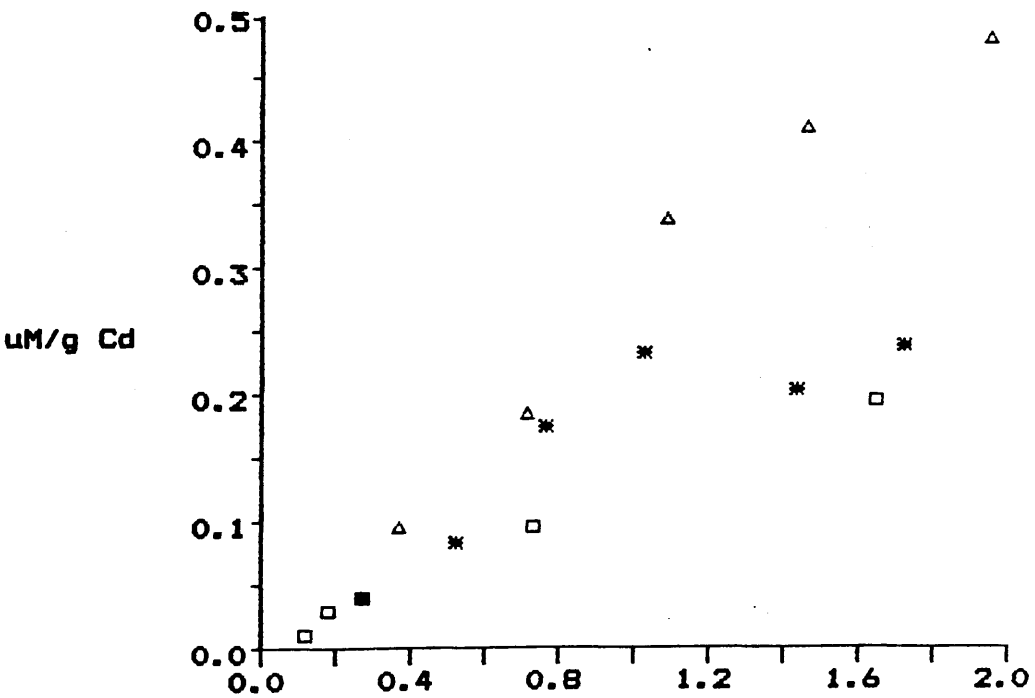
At the equilibrium metal level of 1.5 μM and above, uptake of Cu from SO_4 exceeds that from Cl in the Arkleston soil.

When activities are calculated, only with Arkleston-copper do the SO_4^{2-} -NO_3^- and Cl^- data converge. In the Arkleston High Zinc - Cd system, the NO_3^- and Cl^- data coincide, whilst the SO_4 'splits' from this data and continues in an upwards fashion, whilst the two others level out (Figures 4.6. and 4.7. respectively).

Figure 4.6. Influence of Anion on Cu sorption: Calculated Activities - Ark.

Figure 4.7. Influence of Anion on Cd sorption: Calculated Activities - AHZ.


uM/g Cu
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.06
0.12
0.18
0.24
0.30
Equilibrium Cu activity (uM) - calculated.
Cl - * SO4 - tri. NO3 - sq.
ARKLESTON


uM/g Cd
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.4
0.8
1.2
1.6
2.0
Equilibrium Cd activity (uM) - calculated.
Cl - * SO4 - tri. NO3 - sq.
ARKLESTON HIGH ZINC

The experiment which ran alongside this one aimed to examine the influence straightforward concentration differences were exerting on equilibrium, as all the anion experiments were conducted at a single ionic strength. The graphs relating to this series of determinations are shown in Figures 4.8. (a-c) and 4.9. (a-c) for Cd and Cu, whilst the findings for the concentration effect on uptake and pH are summarized below.

Uptake: Cadmium

Arkleston;	0.0167 M > 0.0333 M > 0.1000 M
Arkleston High Zinc;	0.0167 M > 0.0333 M > 0.1000 M
Fen Arable;	0.0167 M > 0.0333 M > 0.1000 M

Copper:

Arkleston;	0.1000 M ≈ 0.0333 M > 0.167 M
Arkleston High Zinc;	No great effect.
Fen Arable;	No great effect.

In terms of the effect on supernatant pH

Arkleston;	0.0167 M > 0.0333 M > 0.1000 M
Arkleston High Zinc;	0.0167 M > 0.0333 M > 0.1000 M
Fen Arable;	No great influence.

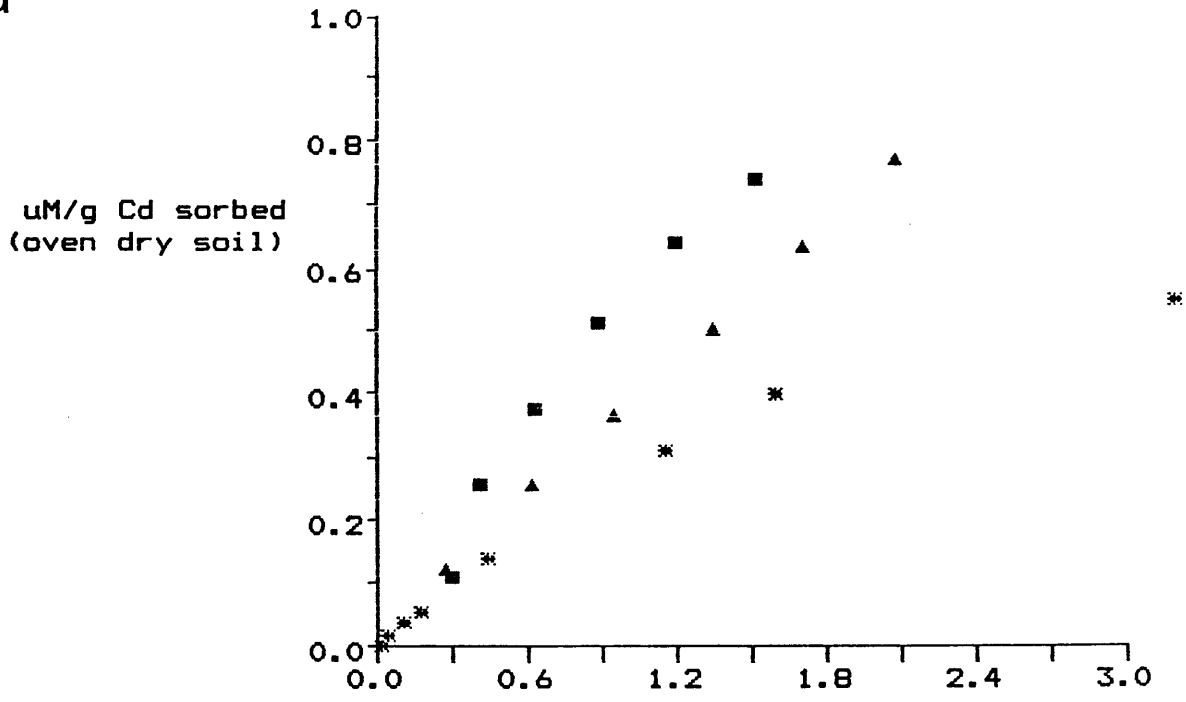
Figure 4.8. Influence of Nitrate Ion Concentration on Cd Sorption.

(a). Ark. (b). AHZ. (c). FA.

Figure 4.9. Influence of Nitrate Ion Concentration on Cu Sorption.

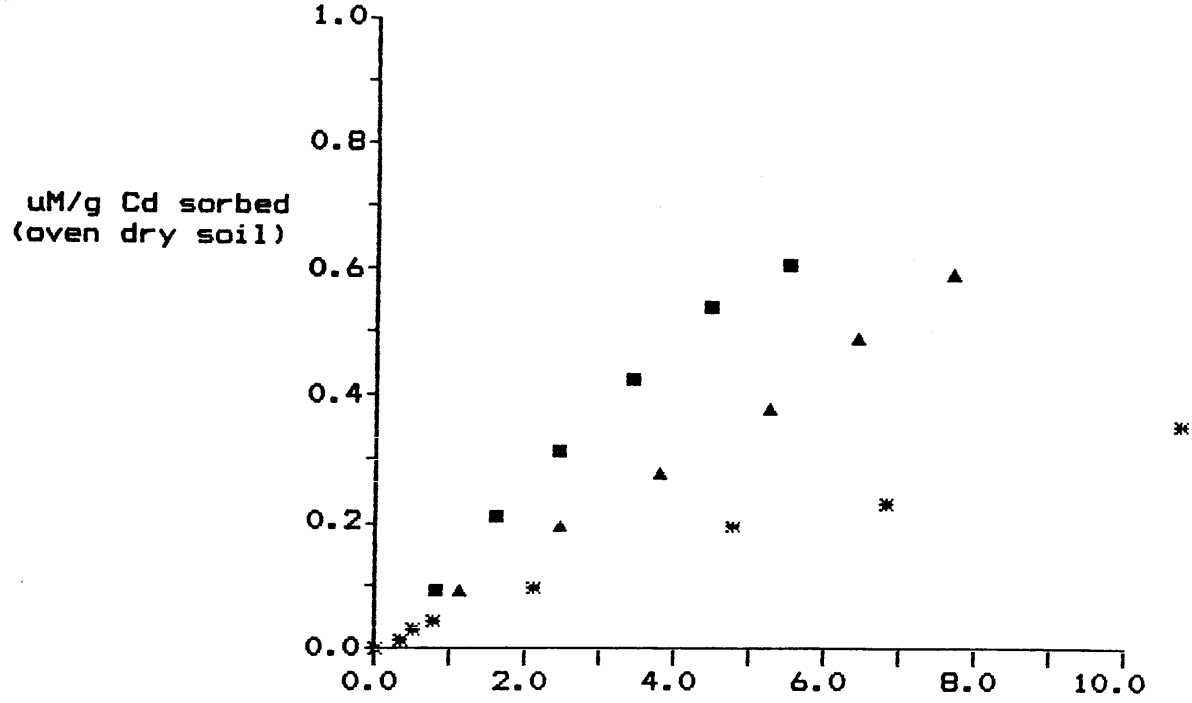
(a). Ark. (b). AHZ. (c). FA.

a



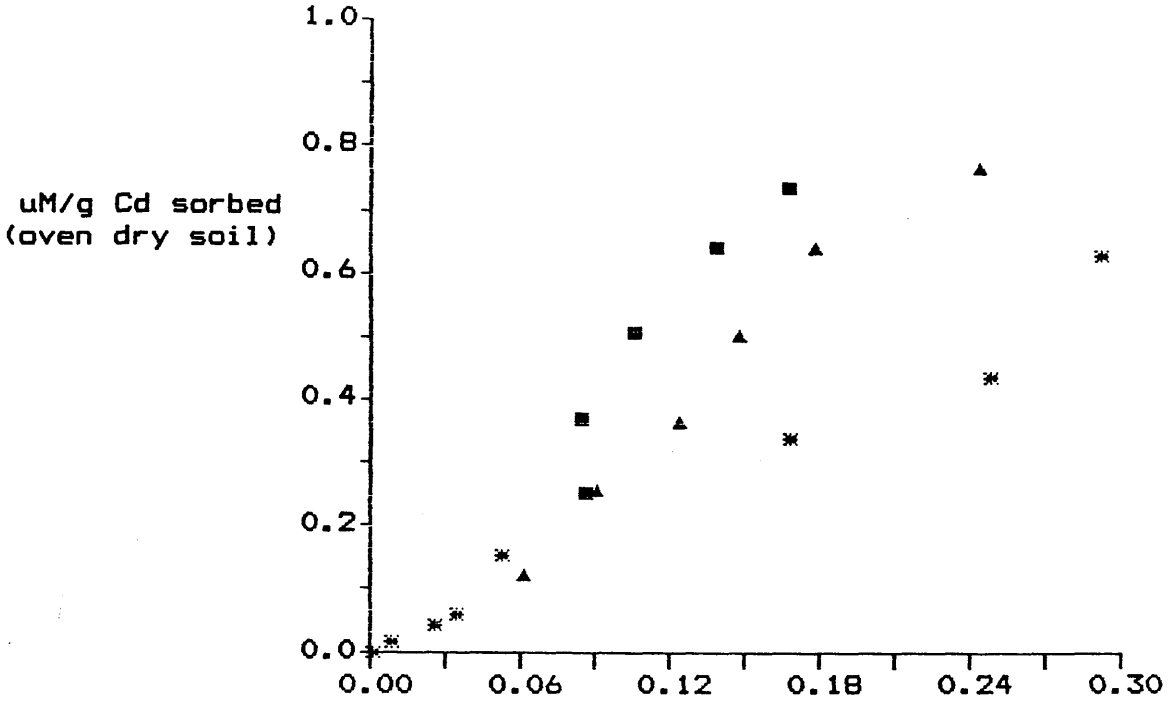
Cadmium in different concentrations of NaNO3.
0.0167M - sq. 0.033M - tri. 0.10M - *
ARKLESTON SOIL.

b



Cadmium in different concentrations of NaNO3.
0.0167M - sq. 0.033M - tri. 0.10M - *
ARKLESTON HIGH ZINC SOIL.

C

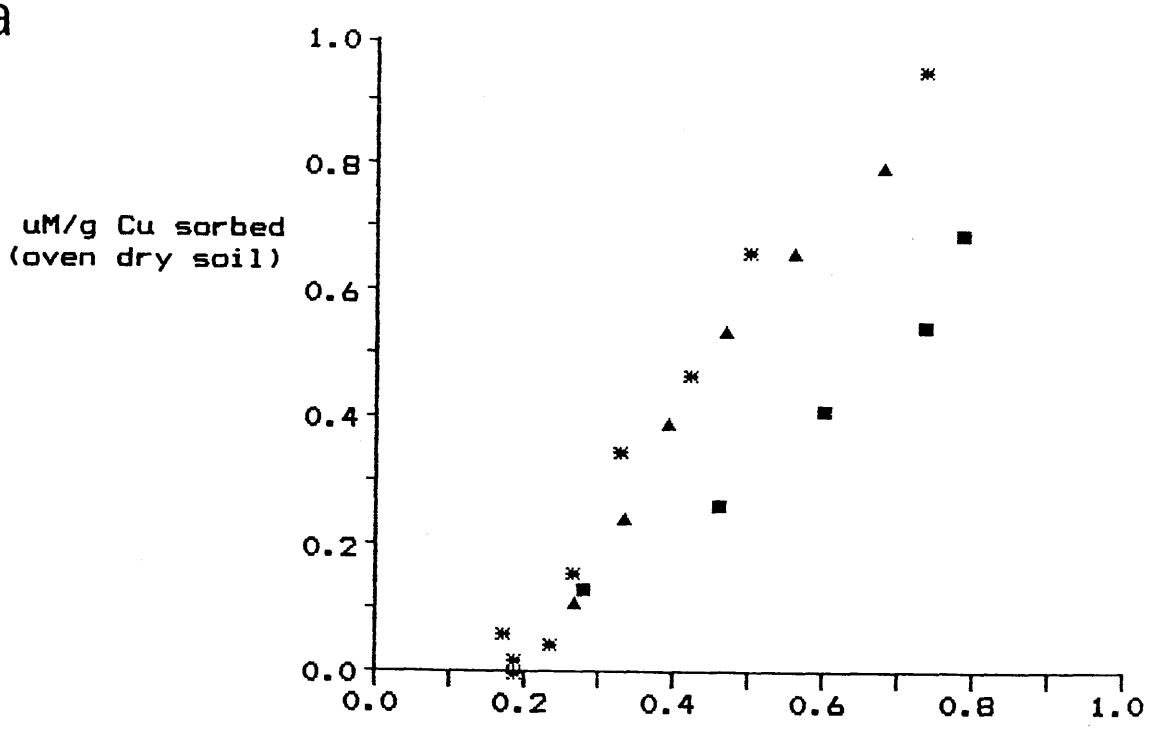


Cadmium in different concentrations of NaNO3.

0.0167M - sq. 0.033M - tri. 0.10M - *

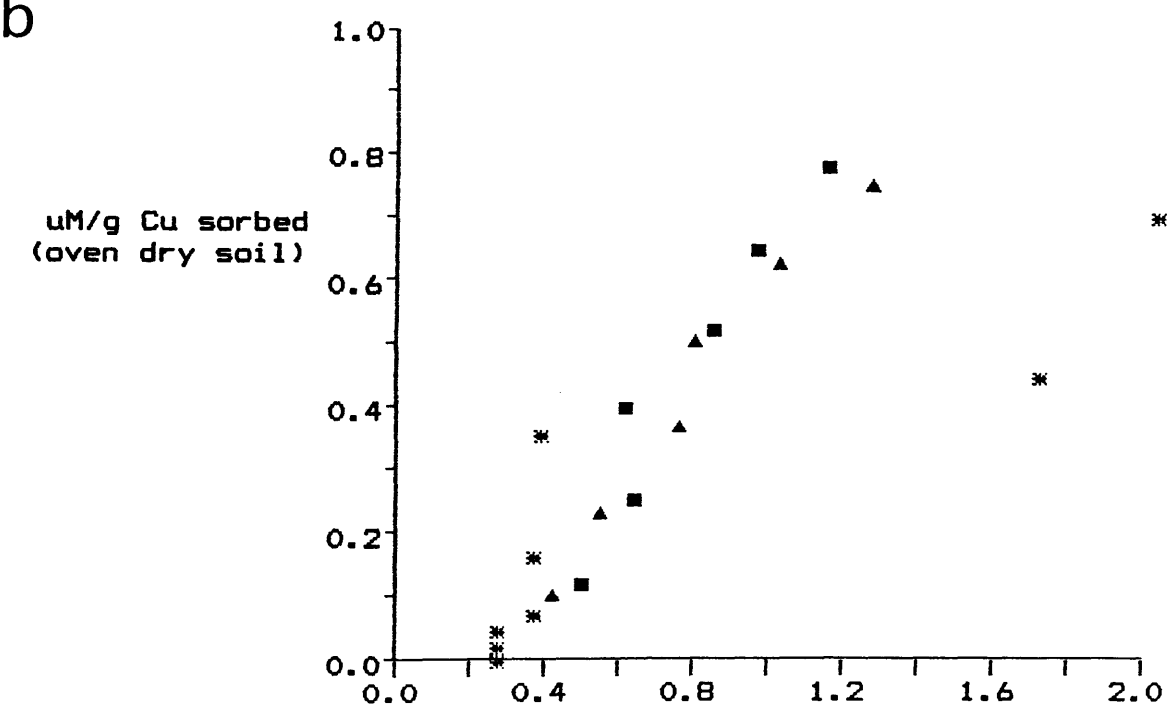
FEN ARABLE SOIL.

a



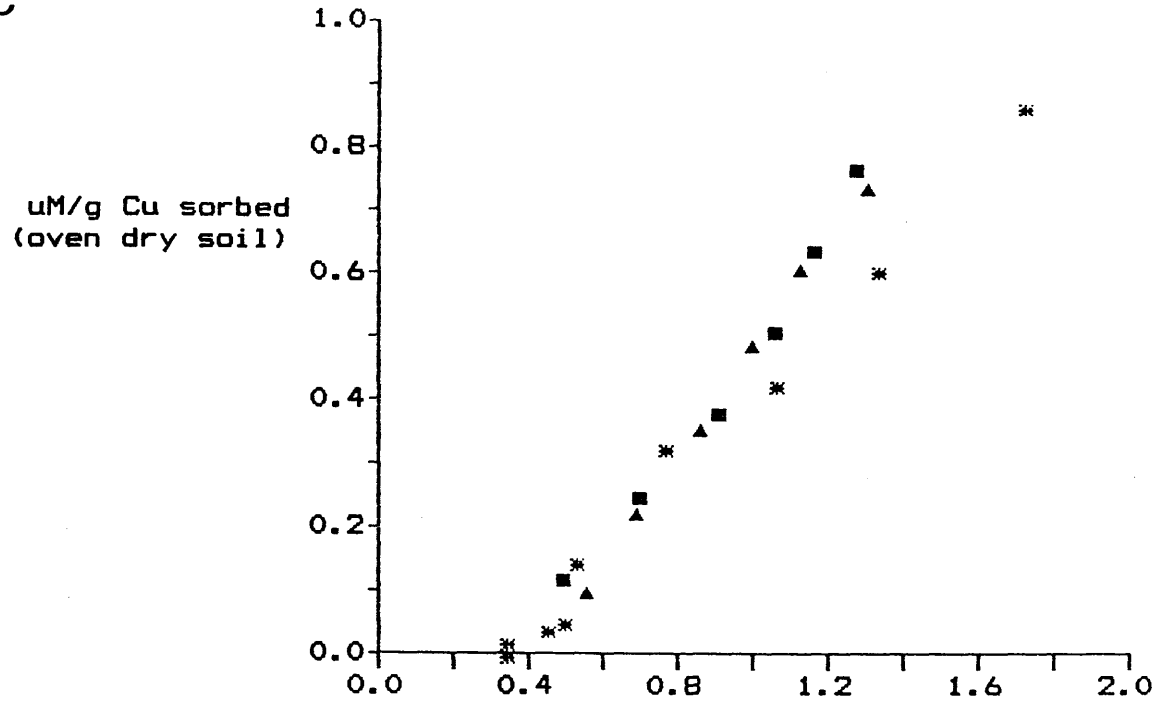
Copper in different concentrations of NaNO3.
0.0167M - sq. 0.033M - tri. 0.10M - *
ARKLESTON SOIL.

b



Copper in different concentrations of NaNO3.
0.0167M - sq. 0.033M - tri. 0.10M - *
ARKLESTON HIGH ZINC SOIL.

C



Copper in different concentrations of NaNO3.

0.0167M - sq. 0.033M - tri. 0.10M - *

FEN ARABLE SOIL.

When the results are considered in terms of activity, only the Cd-Arkleston High Zinc and Cu-Arkleston systems fail to show coincidence of the 0.1, 0.033 and 0.0167 M $NaNO_3$ lines.

The activities of the free metal ions were calculated using the equations and programs in appendix 1, and the chloride, sulphate and citrate pH versus (the proportion of a given species) are illustrated graphically in figures 4.10. (a & b), 4.11. (a & b) and 4.12. (a & b) for both cadmium and copper. These constructions also some idea as to the nature of the solution composition in each of the systems chosen for study. From such considerations it is expected that, between pH 4 and pH 8, the complexed metal forms which predominate will be;

Copper; Citrate > SO_4^{2-} > NO_3^- > Cl^-

Cadmium; Citrate > SO_4^{2-} > Cl^- > NO_3^-

Figure 4.10. Change in Proportions of Species Present in solution with pH: Chloride systems., I=0.1, $pCO_2=10^{-3.52}$ atm.

(a). Copper. (b). Cadmium.

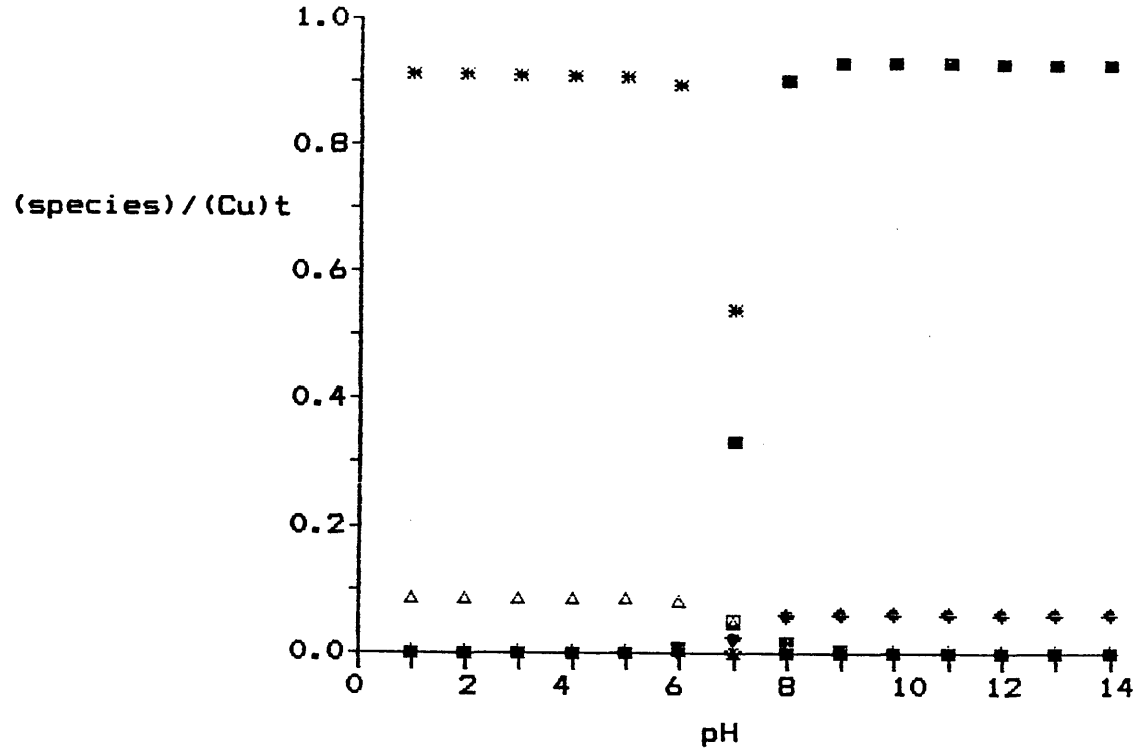
Figure 4.11. Change in Proportions of Species Present in solution with pH: Sulphate systems., I=0.1, $pCO_2=10^{-3.52}$ atm.

(a). Copper. (b). Cadmium.

Figure 4.12. Change in Proportions of Species Present in solution with pH: Citrate systems., I=0.1, $pCO_2=10^{-3.52}$ atm.

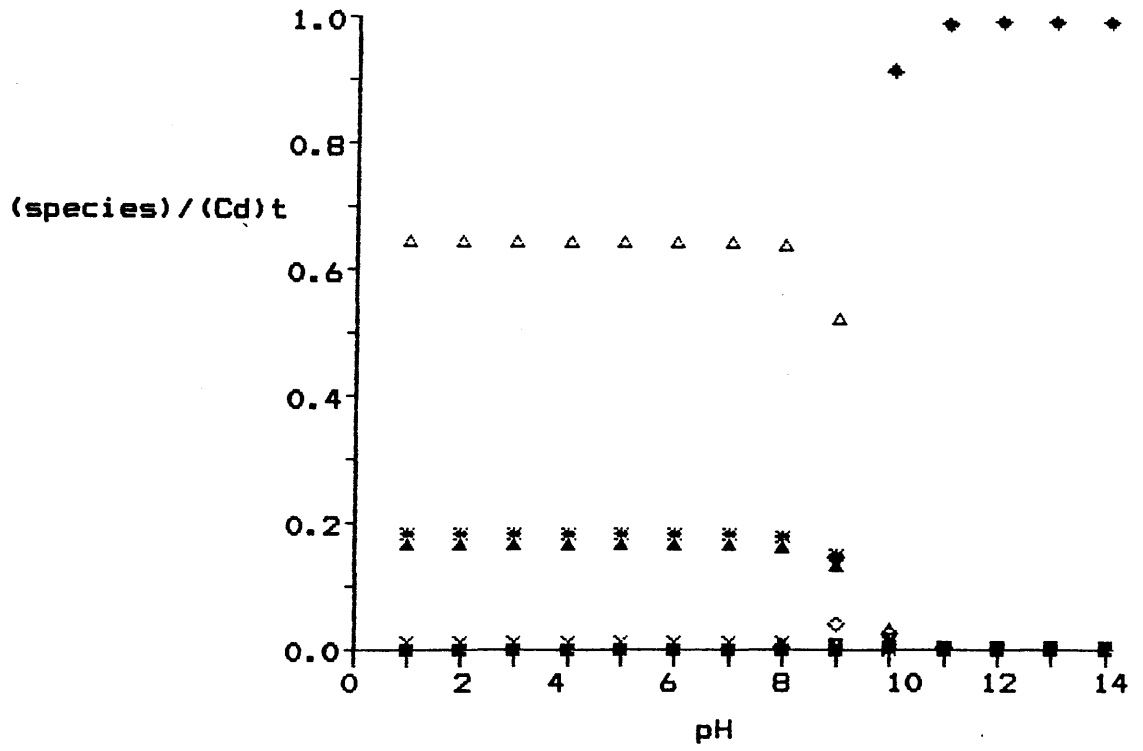
(a). Copper. (b). Cadmium.

a



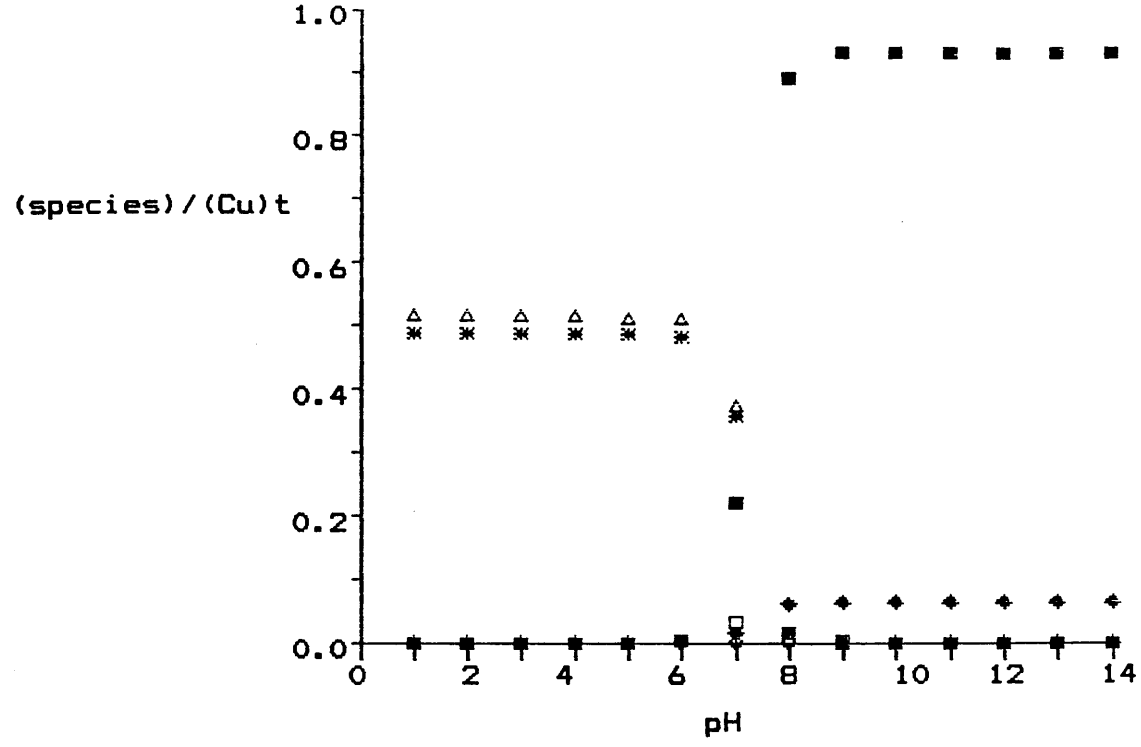
Cu species distribution in NaCl (I=0.1).
Cu - * HO1 - open sq. HO2 - sq.
HCO3 - open dia. CO3 - dia. Cl1 - open tri.
Cl2 - tri.

b



Cd species distribution in NaCl (I=0.1).
Cd - * HO1 - open sq. HO2 - sq.
HCO3 - open dia. CO3 - dia. Cl1 - open tri.
Cl2 - tri. Cl3 - x Cl4 - +.

a

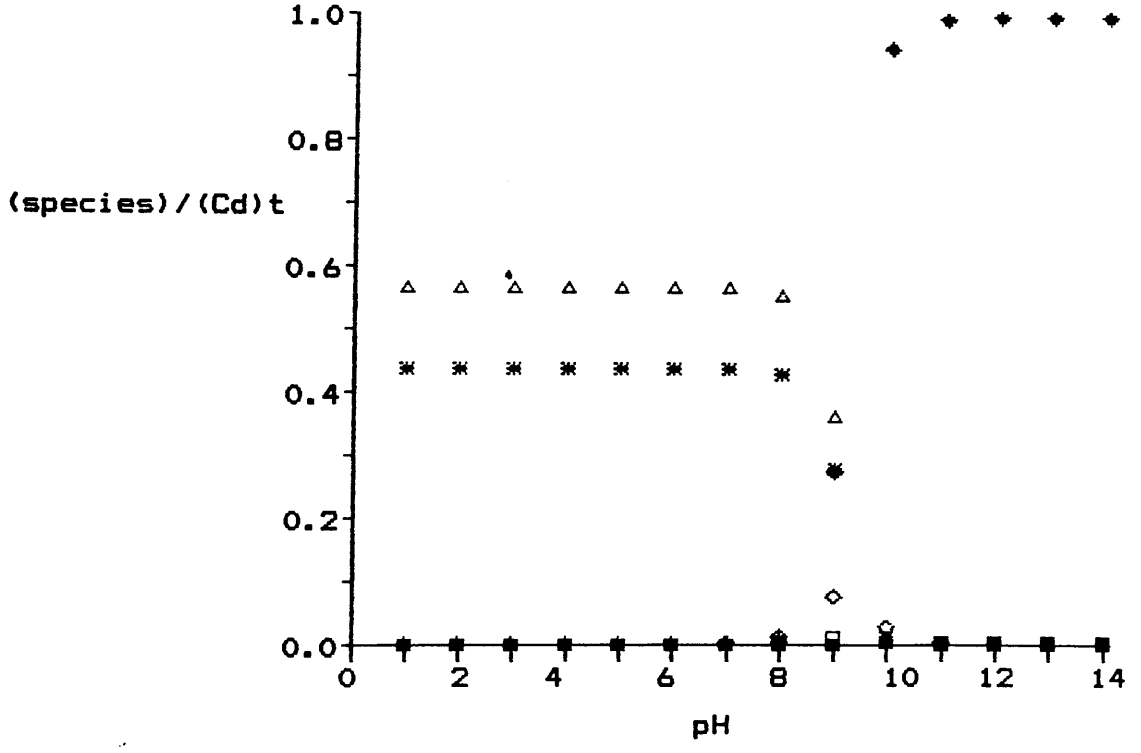


Cu species distribution in Na2SO4 (I=0.1).

Cu - * HO1 - open sq. HO2 - sq.

HCO3 - open dia. CO3 - dia. SO4 - open tri.

b

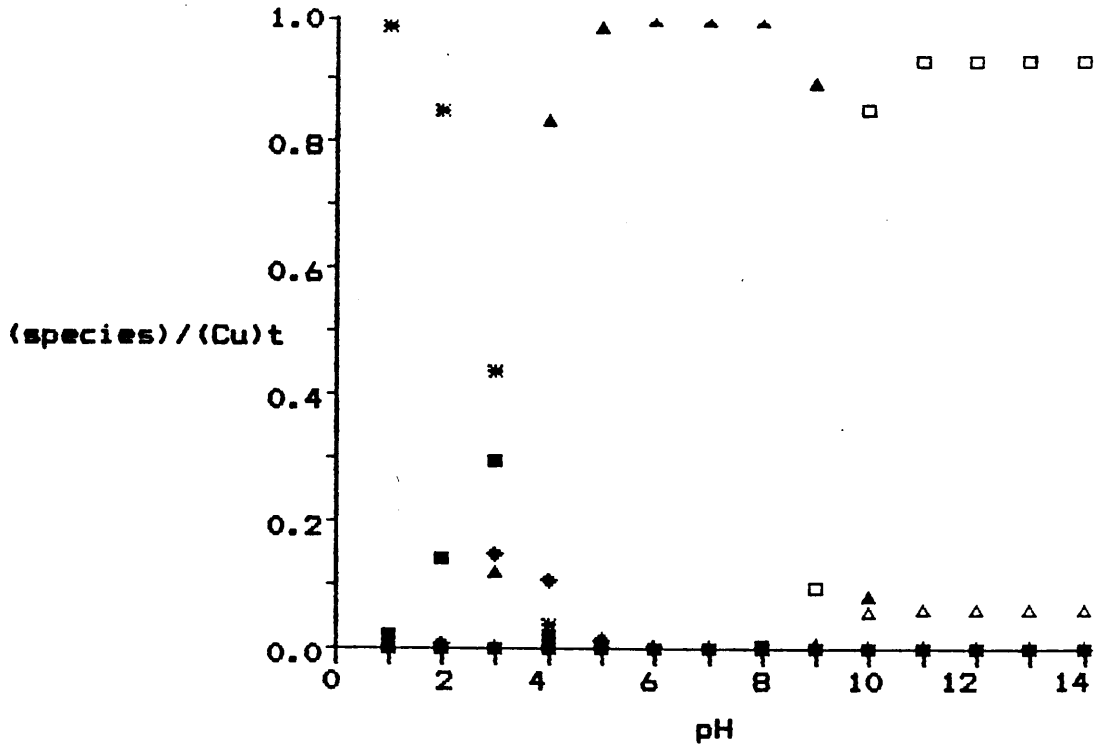


Cd species distribution in Na2SO4 (I=0.1).

Cd - * HO1 - open sq. HO2 - sq.

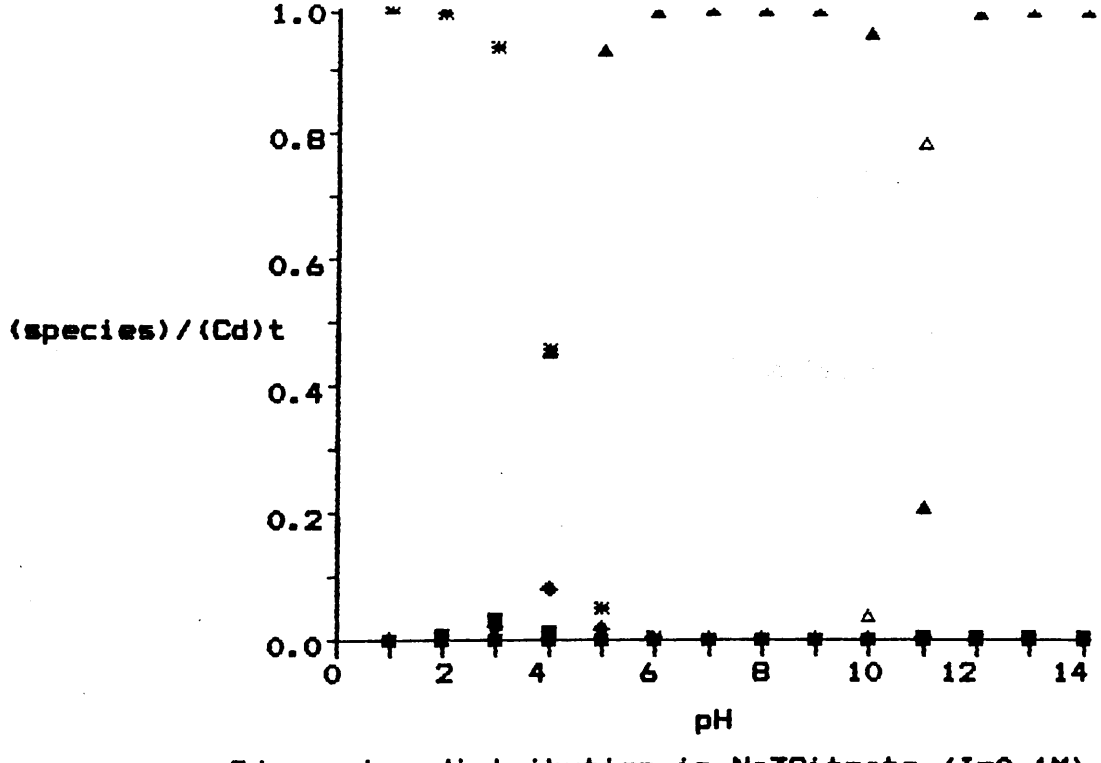
HCO3 - open dia. CO3 - dia. SO4 - open tri.

a



Cu species distribution in Na3Citrate (I=0.1M).
Cu - * HO1 - + HO2 - open sq. HCO3 - open dia.
CO3 - open tri. H2L - sq. HL - dia. L - tri.

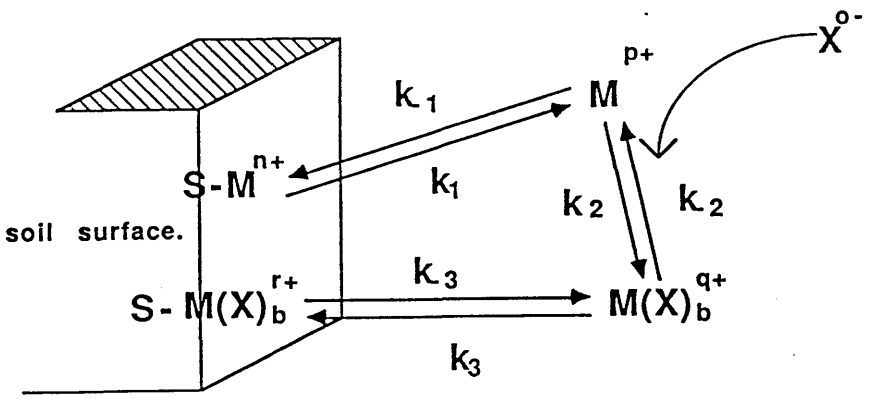
b



Cd species distribution in Na3Citrate (I=0.1M).
Cd - * HO1 - + HO2 - open sq. HCO3 - open dia.
CO3 - open tri. H2L - sq. HL - dia. L - tri.

Hence, it is expected that if the affinity of these ligands is greater than the affinity for the soil, and that the ion-pairs and hydroxy-species do not sorb onto the soil, that the amount of metal sorbed from each system should show the reverse order.

The sorption process depends upon the balance of kinetic and thermodynamic equilibria. If we consider the thermodynamic aspect in isolation, in a simple, single, ligand system;



S = 'surface'. k = rate constant.
M = metal ion. b,o,r,p and q are integers.
X = ligand.

Usually, the only known constant in such a system is K_2, the stability constant for the solution complex. If the tendency for M^{n+} to be sorbed is greater than K_2, then the process (ignoring the rate at which these phenomena occur) should move towards this end. If $K_2 > K_3$, and $K_2 > K_1$, then the majority of the metal will remain, complexed, in solution. Thus, depending upon the status of the system, we can surmise the magnitude of the stability constants with respect to the soil and solution complexes. Any observation

which we make will include a time factor ie. if we say that because M^{n+} is the major solution component in the experiments, then that statement has to be qualified by stating the time in which such an observation was made.

The use of different background electrolytes by other authors to provide competition with the soil for metals has shown various trends. The influence of organic material, whether it be in the form of a discrete well characterized molecule such as EDTA (Checkai *et al*, 1987) or the more heterogeneous materials found in sludges etc. (Minnich *et al*, 1987; Neal and Sposito, 1988) or simply the native soil/sediment materials (M^{c}Bride and Blasiak, 1979; van den Berg *et al*, 1987) has been shown to enhance the mobility and increase the solution levels of trace metals, very much in agreement with the findings of this study. The studies of Schnitzer and Skinner (1966), Stevenson (1977), van den Berg *et al* (1987) and Mench *et al* (1988) have clearly demonstrated the potential stability of soil organo-metallic complexes. Senesi and Sposito (1989) have shown that the complexes formed from leaf litter and Cu^{2+} is a very stable inner-sphere one.

Where inorganic interactions are concerned, the consensus opinion is that Cl^{-} is very influential in mobilizing Cd^{2+}, and, to a lesser extent Cu^{2+} (Doner (1978), Soon (1981), O'Connor *et al* (1984), Petruzzelli *et al* (1985) and Hirsch *et al* (1989)), which, for Cd is in agreement with what is found in this work. Considering other ligands and Cu, the situation is less clear cut: even the Cd findings contradict the expectations of any speciation considerations. Although Garcia-Miragaya and Page (1976) mentioned that there is little spectroscopic evidence that $(CdSO_4)^0$ forms in solution, whilst O'Connor

et al (1984) compared Cd uptake in SO_4^{2-}, ClO_4^- and Cl^-, and showed minimal influence of SO_4^{2-} on levels of Cd^{2+} in comparison to ClO_4^- which is presumed to interact with cations only very slightly. Nitrate is often though of as interacting only marginally with solution ions, but the copper results suggest that, certainly relative to chloride, NO_3^- seems to be having some enhancing influence on the solution levels of Cu: In all cases, the results of this work, for Cu, agree with the expectations given by the speciation considerations (the Arkleston High Zinc points are subject to scatter, though, and are thus open to debate).

Using the different electrolytes and electrolyte concentrations has a further consequence over and above the prime influence of the anion and that is the influence on the system pH. Given the sequence quoted in the anion experiments, it would be expected that if pH (and its influence upon surface and solution speciation) were playing a role in the uptake process, then soil retention would be enhanced, in the same order. Similarly for the concentration comparison, that the low concentration system sorbs the most M^{n+} whilst the high concentration system sorbs the least. With the anion experiments, the expected pH influence is almost completely reversed, indicating that the perceived effect is almost solely due to the different anions. Considering the concentration tests, the Cd systems follow the pH trend exactly.

pH can influence sorption in several ways;

Enhancing Effect -

(a). Precipitation.

(b). More negative sites if the pH rises.

(c). Changes in solution speciation.

Diminishing Effect -

(a). Al^{3+}, Fe^{3+}, Mn^{3+} etc. release on pH decline due to competition.

(b) H^+ competition.

(c) lower pH, sites become more positive.

(d) pH rises, organic matter solubility is enhanced, keeping metal ions in solution.

Despite this, Cu uptake seems to be completely independent of concentration of the nitrate anion. Speculatively, it might be suggested that the changes in the surface charge brought about by the alterations to the pH in these systems (bearing in mind the pH speciation insensitivity of Cd) greatly influence the sorption of Cd species, whilst the solution complexes of Cu remain relatively unaffected, recalling the direct relationship of soluble organic material and pH.

Examining the sets of data, in terms of the calculated speciation, sheds some more light on the influence that the solution components are exerting on Cu and Cd. When the anion data is plotted in terms of activity versus amount of metal sorbed, if the calculation is managing to accommodate all the important species, then regardless of the system, the data points ($(Cu^{2+})_{free}$ and $(Cd^{2+})_{free}$) should converge. This also presumes that the species, other than the free-ion, do not sorb. The speciation calculations do not attempt to account for the surface interactions and also the organic component of the solution phase. If no convergence results, then the converse of this argument is that the other species sorb to varying degrees and that the surface of the sorbing material is influenced to such an extent that certain species are taken up in preference to others. Obviously, the speciation calculation may not be entirely

comprehensive and correct; but, if as mentioned with respect to Jarvis and Jones (1986), that the solution organic component is of such high stability that it can effectively be ignored from speciation calculations, allowing the inorganic species description to be applied to the solution, the only remaining options to explain sorption differences are changes in the surface speciation and sorption of other species: the formation of an ion-pair may reduce the electrostatic impetus for surface-solute interaction, however, the new complex may be sterically more suited to uptake - indeed, as the following discussion shows, complex formation could be viewed as being catalytic with respect to sorption.

The Langmuir expression is essentially a first order kinetic expression,

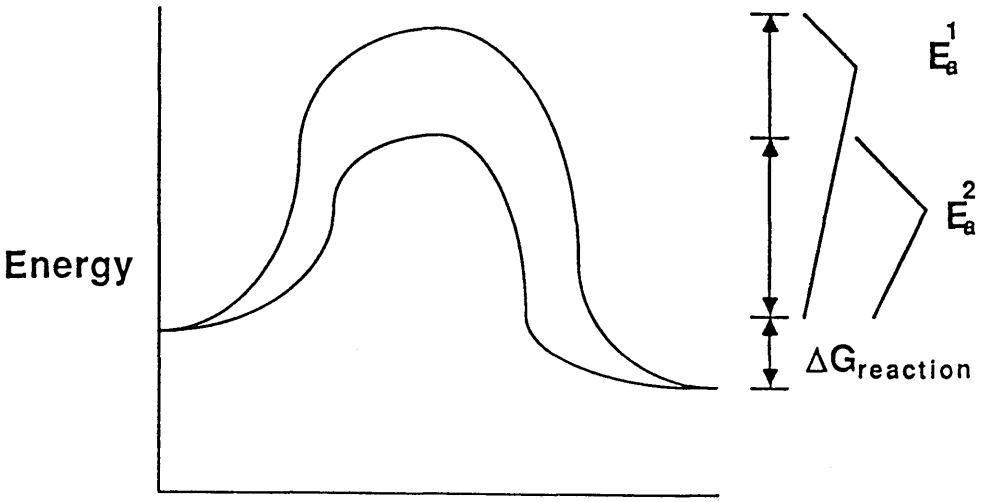
$$X = \frac{X_{max} \cdot K \cdot C}{1 + K \cdot C}$$

Thus, for any reaction which it describes, although the thermodynamic interpretation may be redundant, there is the likelihood of the description of the kinetics of the process: *viz*

$$A + B \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} AB$$

This overall constant is what the original Langmuir "bonding" constant is based on, and correctly applied has some thermodynamic credence. Like the Michaelis-Menten equation, the poise of a given reaction is a balance of forward and back reactions. In an analogous manner, as an enzyme can catalyze a reaction by reducing the activation energy, the reaction of an ion with a surface may be subject, whilst not precisely to catalysis (as in this instance the reaction mediator is used up - an irreversible

or poisoned catalyst) does result in a reaction proceeding more favourably.



Extent of Reaction.

E_a^1 - uncatalysed activation energy.

E_a^2 - catalysed activation energy.

Such a diagram may describe such a reaction as this;

$$Cu^{2+}_{(aq)} + 2\ Cl^-_{(aq)} + Surface_{(s)} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} (CuCl_2\text{-}Surface)_{(s)}$$

Whilst $Cu^{2+}_{(aq)} + Surface_{(s)} \rightleftharpoons (Cu\text{-}Surface)^{2+}_{(s)}$ does not proceed so rapidly. Could Cl^- be acting as a catalyst?

At the moment this is conjecture, but it presents an interesting side to the investigation of sorption reactions, combining an appreciation of both kinetics and thermodynamics; only in the models of Barrow (1987) has an effort been made to describe both aspects of the phenomenon.

With this first set of data, a degree of agreement between the data sets in terms of the free ion activity is observed only with two of the soils. In the Arkleston-Cu system, the NO_3^-, SO_4^{2-} and Cl^- data coincided when the Cupric ion activity was taken as the sorption variable,

whilst in the Cd-Arkleston High Zinc system, the NO_3^-, SO_4^{2-} and Cl^- initially converge, but at approximately 0.25 μM Cd/g, the nitrate and chloride data reach a plateau, whilst the sulphate isotherm continued upwards. Both the Cl^- and

*However, the stability and existence of the ($CdSO_4^0$) species is uncertain; the use of another stability constant may have led to a different interpretation of the results.

With the AHZ soil, the view presented in the original text is far from definite, it must not be forgotten that the various species are in equilibrium with one another and the distribution of the chemical species is not static.

If the sorption patterns are related to the balance of constants diagram at the beginning of this discussion, the change in priority of ligands, in terms of enhanced or diminished uptake as $[M^{n+P}]$ is increased, is a reflection of the stability constants governing these reactions. It can be seen that the formation of a given complex can ultimately be related to the metal concentration in solution:

$$K = \frac{(M.X)^{(l-n)+}}{(M^{n+})(X^{l-})}$$

Performing the 'anion' experiments in a slightly different form gives some more information regarding the nature of the reactions occurring in the equilibrations. In the second series of experiments, the uptake measurements were performed in systems which differed in concentration of a single background electrolyte. The speciation calculations performed with the 'anion' experiments yield values for free metal activities which are essentially stripped of their dependence on pH and concentration. This second series of determinations should confirm that the observed differences in uptake patterns are anion specific, and not

just a concentration phenomena.

In systems where the electrolyte ratios were 6:2:1, there is surprisingly little influence on either Cu or Cd (see figures 4.8. a-c and 4.9. a-c respectively) removal from solution. This area has been little investigated, and the only references to it are contradictory; Gambus (1987) states that [Cl^-] is a major influence on Cd uptake (uptake $\propto$ 1/[Cl^-]), whilst both Elrashidi & O'Connor (1982) and Shuman (1986) and found that I had little or no effect on Zn sorption.

The pH influence is such that we would expect there to be a minimal change in the uptake characteristics of Cu and Cd by the Fen soil, and that this is, indeed, what is found with the Cu system. In the two more acidic soils, the pH follows the pattern we would expect presuming that increasing I, by a mass action affect, displaces protons into solution, and hence by virtue of the pH and [NO_3^-] influence, we expect that uptake $\propto$ 1/[NO_3^-] . Whilst Arkleston High Zinc showed no alteration on moving from 0.1 - 0.167 $NaNO_3$, Arkleston exhibited precisely the opposite pattern to that which was predicted. Even when considering the systems in terms of activities, these patterns persisted, so it must be concluded, that in the Arkleston system, nitrate complexes are taken up more avidly than free metal ions. Where no great influence is present, then we must concur with Sposito (1982) who states that this is evidence of highly specific sorption. These phenomena also continue through the species adjusted calculations, see figures 4.13 (a-c). and 4.14. (a-c).

The Cd systems followed the predicted pattern, indicating the greater stability of the solution complex over the soil-bound complex. The speciation considerations,

shown in figure 4.13. (a-c), display the disappearance of the influences shown in the concentration isotherms, except in the Arkleston High Zinc system. From this we can state that the uptake of some NO_3^- complexes and changes in the surface charge are influencing Cd uptake in the Arkleston High Zinc system, whilst in the other two we are dealing with pH and solution complexation effects. The uptake of a monovalent Cu species has been proposed by Lewis and Broadbent (1961), whilst, if we can draw an analogy between the two elements, Zachara *et al* (1988) mooted the presence of a mono-valent Zn form in sorption experiments on $CaCO_3$.

In the Cd systems, at low solution concentrations, the effect of the anion concentration appears to be diminishing, and it seems as though the experimental lines begin to converge.

Chloride, sulphate and nitrate are hard bases, thus we expect greater pairing with Cu than with Cd (the former a borderline acid, the latter a soft acid), and hence, that these ligands should exert more of an influence upon the solution chemistry of Cu than Cd. The majority of soil ligands will be 'O' ones: it could be that Cl^- is soft relative to these and hence the Cd-Cl anomaly with respect to its uptake, in that more is taken up in the sulphate than in the chloride systems - in this instance, the HSAB principle prevails over the thermodynamic stability constant. Cu should display equivalent affinity (in HSAB terms) for the solution and surface ligands - certainly it would seem that Cu uptake is lowest in the systems with 'O' bearing ligands, which would confirm that Cl^- is a softer base than either of the anions used, or any of the surface groups.

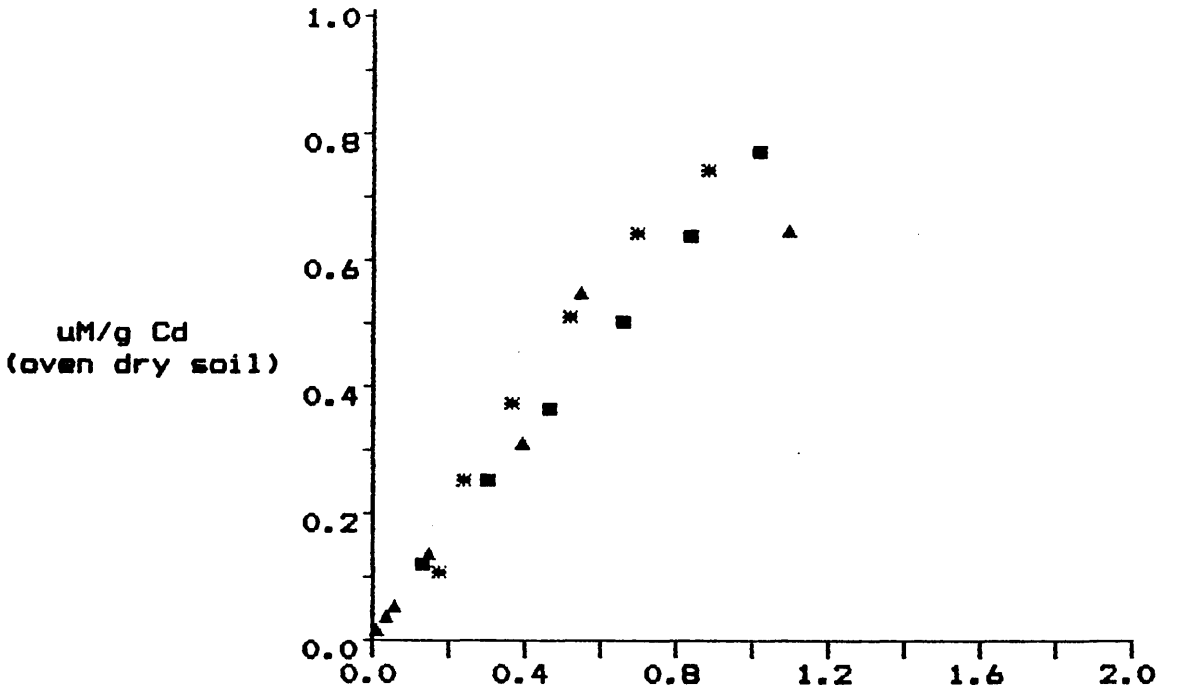
Figure 4.13. Influence of Nitrate Concentration on Cd Sorption: Calculated Activities.

(a). Ark. (b). AHZ. (c). FA.

Figure 4.14. Influence of Nitrate Concentration on Cu Sorption: Calculated Activities.

(a). Ark. (b). AHZ. (c). FA.

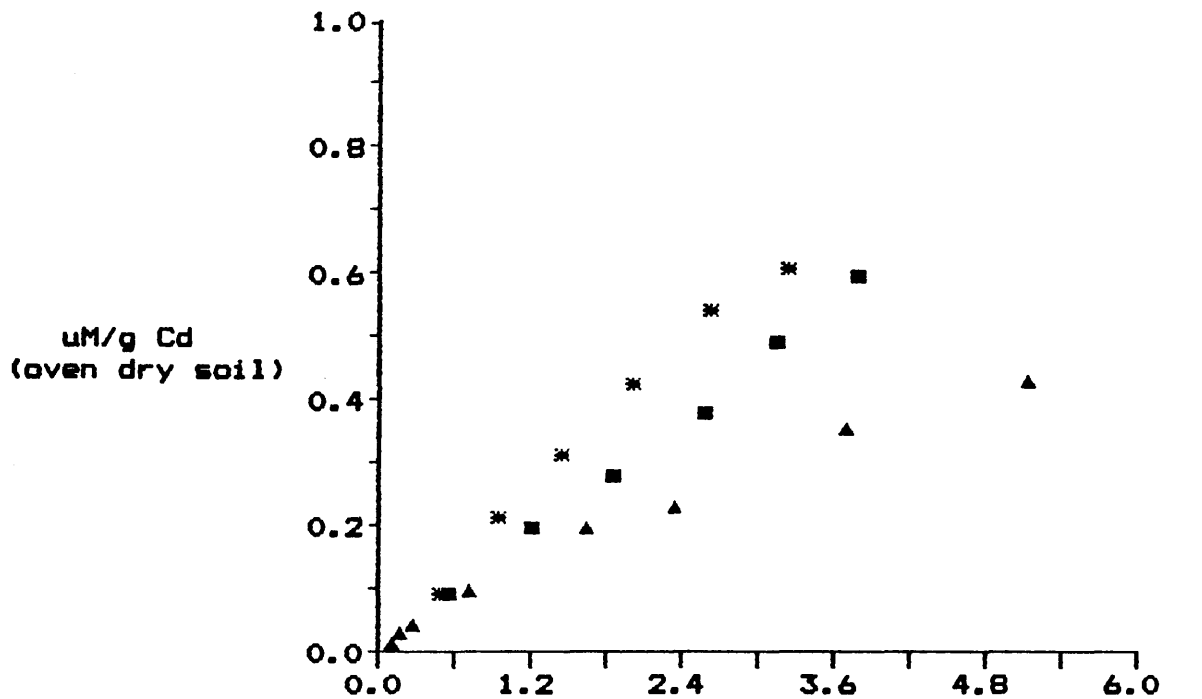
a



Calculated activity in 0.0167M (*), 0.0333M (sq.)
and 0.1000M (tri.) NaNO3.

ARKLESTON

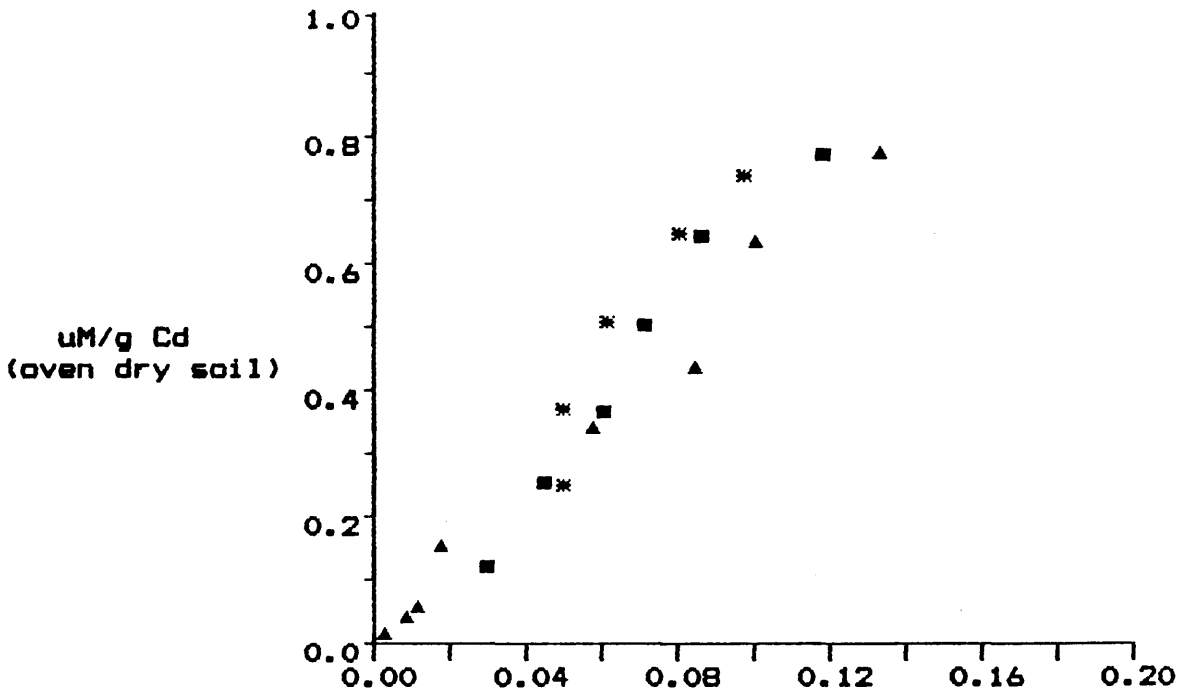
b



Calculated activity in 0.0167M (*), 0.0333M (sq.)
and 0.1000M (tri.) NaNO3.

ARKLESTON HIGH ZINC

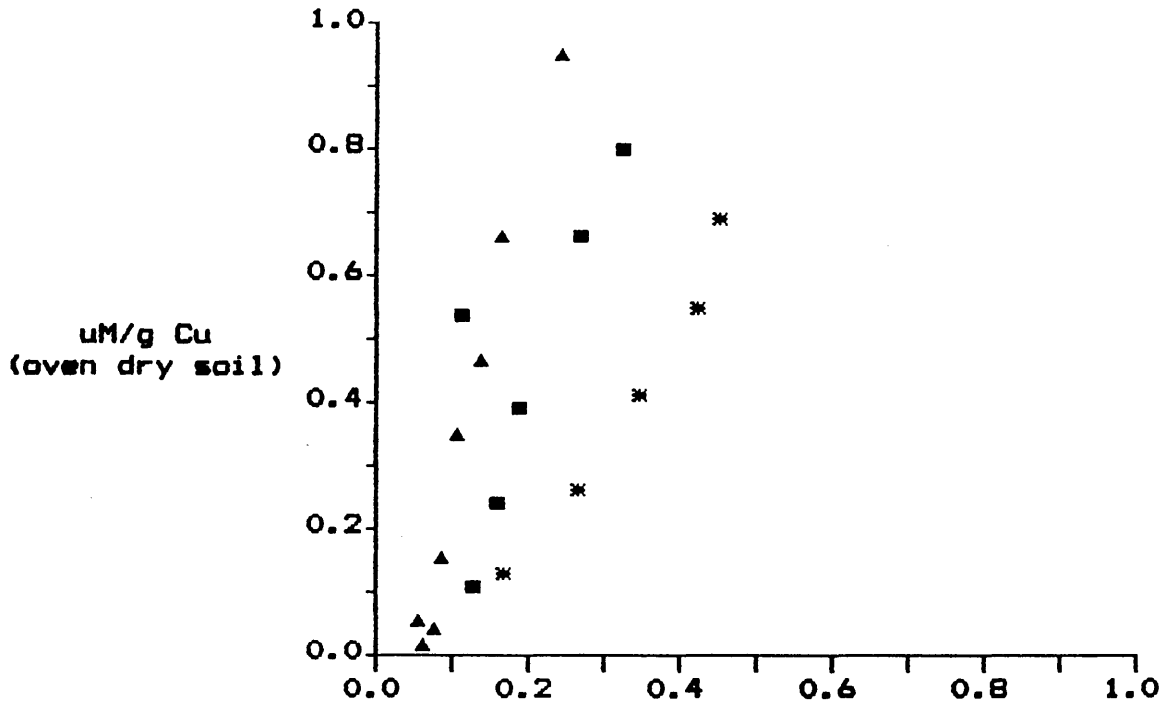
C



Calculated activity in 0.0167M (*), 0.0333M (sq.) and 0.1000M (tri.) NaNO3.

FEN ARABLE

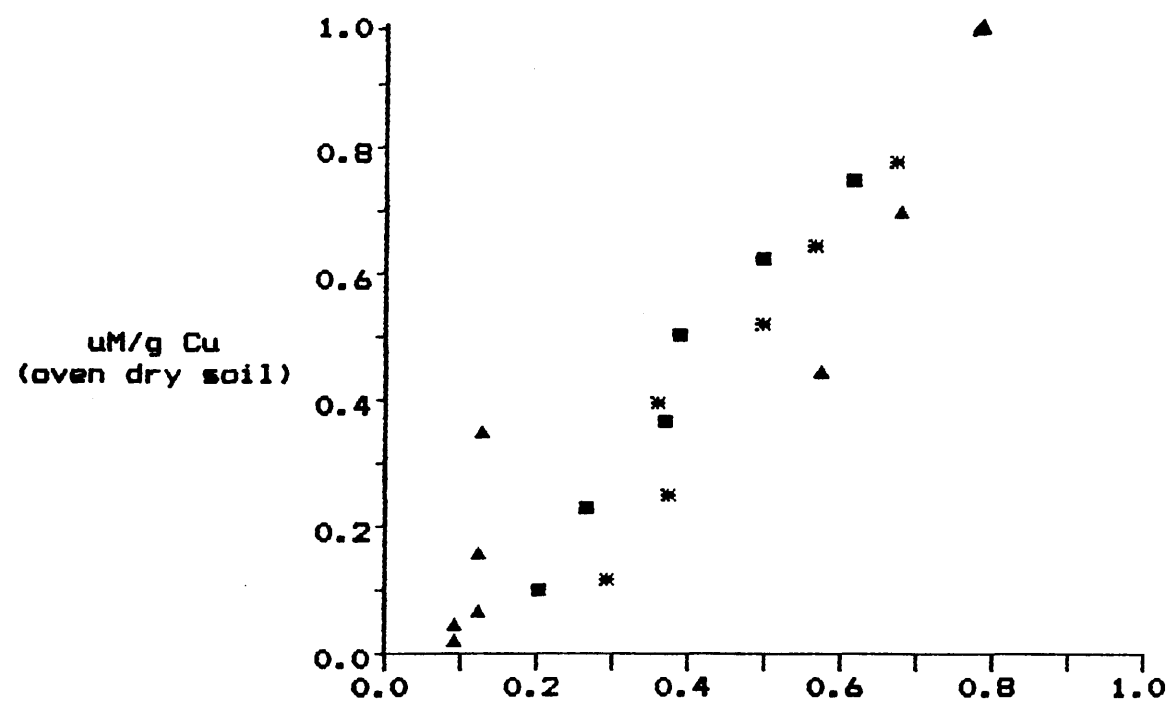
a



Calculated activity in 0.0167M (*), 0.0333M (sq.) and 0.1000M (tri.) NaNO3.

ARKLESTON

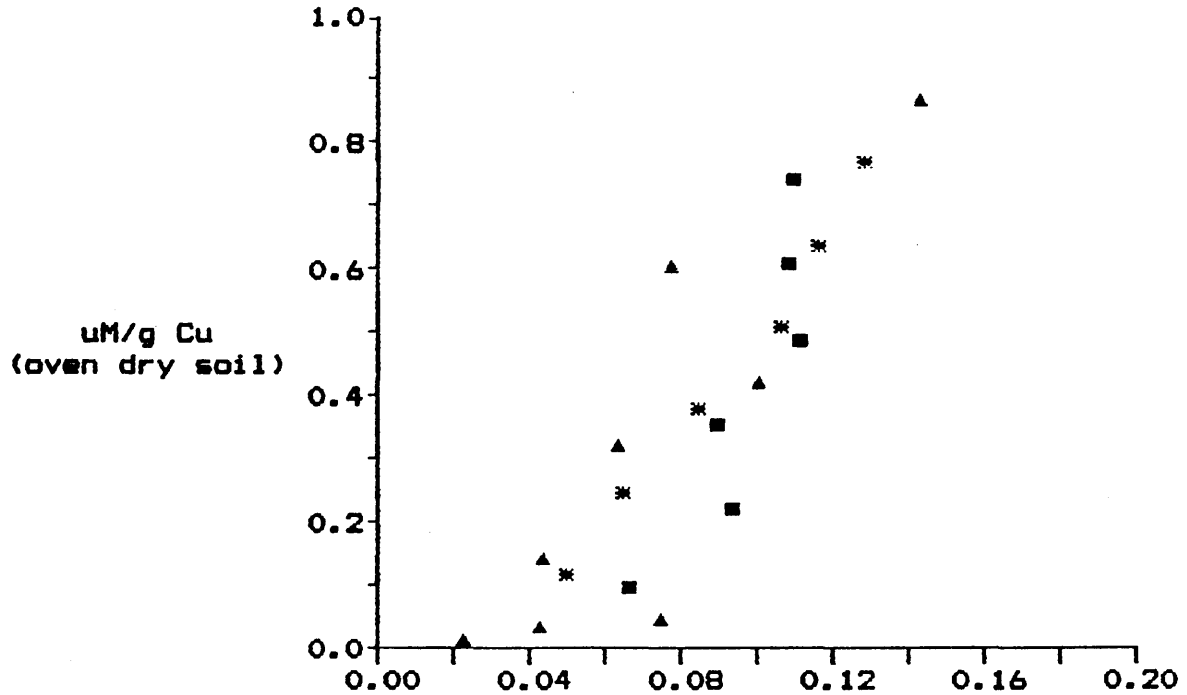
b



Calculated activity in 0.0167M (*), 0.0333M (sq.) and 0.1000M (tri.) NaNO3.

ARKLESTON HIGH ZINC

C



Calculated activity in 0.0167M (*), 0.0333M (sq.) and 0.1000M (tri.) NaNO3.

FEN ARABLE

4.4. Overview of Chapter 4.

Cations

In this area, the presentation of the results is a problem, visual representation suggests no influence on Cd uptake of K, Fe, Pb, Zn and Cu, even when all are added at once. In the Cu systems there seems to be a definite influence of Cd, and perhaps from Zn and the combination of ions.

The mathematical analysis shows quite a difference in the competitive effect from that seen in the visual appraisal. It is difficult to assess where to draw the boundary of what is and what is not a significant effect, although, in both the Cu and Cd systems, the S (%) values surely point to the effect being real. The common ground in the two approaches is that Cd/Zn are the best Cu uptake retardants.

Thus, if we are finding that even at these low levels, Cu is demonstrating increased mobility, this has implications for the addition of metal bearing wastes to soils, in terms of (a) bioavailability, and (b) pollution of groundwater supplies. There is a need to investigate the influence of differing ratios of metals to truly evaluate the competitive effects. There is also the need to perform similar studies on larger sample numbers to enable a more rigorous statistical analysis the opportunity to shed light on the phenomena.

Anions and Concentration.

The difference between the sorption in the ΔC and in the $(\Delta C + \Delta I)$ experiments is great enough to suggest specific ions affect the sorption of Cu and Cd in different ways. The

stated importance of organic ligands (from the previous chapter) in enhancing solution metal levels has been indicated by the set of experiments using the citrate anion. The inorganic ligands have variable influences, but a general trend is that Cl^- will increase the mobility of Cd, whilst SO_4^{2-} will do much the same with copper: one major point to note is that it is not sufficient to consider thermodynamic stability constants alone in considering what will happen to a metal in the presence of a given ligand. The differences between the anion systems even when activities are considered suggest that ion-pairs may be being sorbed, particularly in the Cu - (ΔC + ΔI) systems, where increasing the levels of NO_3^- in fact increased, in some situations, the amount of metal sorbed.

Clearly, the implications here are in terms of changing bioavailability: increasing solution organic materials, such as could be given by adding sewage materials, reduces sorption, as shown by Brown *et al* (1989) for Cd, and could thus act as a solution reservoir for more labile easier plant sorbed species, (In areas which derive their water supplies from groundwater sources, enhanced leaching capacity of EEC Red list materials such as Cd, and possibly Cu, may even have environmental health implications) despite the effect which this had on the pH of the systems.

Increasing concentrations of a given anion have a marginal effect on the sorption of free metal, and, as the total uptake showed only small differences, it may be assumed that metal uptake, at these low metal levels, is proceeding in a highly specific manner; Charlet and Sposito (1989) suggest that such behaviour is indicative of the formation of inner-sphere complexes.

Nitrate containing fertilizer materials may reduce the

movement of Cu while enhancing the mobility of Cd, whilst a chloride containing one would very much increase the mobility of Cd - the anion composition of a sludge material will thus be of greater importance in the mobility considerations (Singh *et al* (1988) has shown that increasing inorganic soil N increased plant Cd, attributed to the greater bioavailability in these circumstances).

Chapter 5. Electrochemical Studies of Soil Cadmium and Copper.

5.1. Scope and Use of Potentiometric Analysis.

In chapter 4 it was observed that selectivity sequences will be, to an extent, dependent upon the time within which the observations are made, due to differing reaction kinetics of various species. The independence of the change in 'free' ion activity with respect to the total metal sorption was also commented upon. With these observations in mind, a series of titrimetric examinations were conducted using the ion-selective electrodes.

Reactions in soils have benefitted greatly from an understanding of the proton interactions with the soil solid and solution components, as monitored by pH electrodes. Potentiometric titrations have been used as the basis for modelling surface reactions (Sculthess and Sparks 1988). Given that models to describe sorption processes have evolved from such analyses, it is curious that such studies have not been mimicked using other electrode systems. Indeed, the use of ISE's *per se* is, in terms of the amount of material found in the literature, rather meagre, particularly in light of the attention paid to the study of ion-activities in soils (Sparks 1984): A lengthy review article by Yu (1985) on the use of electrodes in soil science fails to even refer to the use such tools may have in the study of activities and kinetics of soil reactions. Speciation in biological and environmental systems has been shown to be of great importance (Bernhard *et al* 1986); the ISE is one of the few analytical methods which can be directly applied to the topic. A further possibility for research using ISE's is in dynamic studies of uptake processes, as has been

mentioned, the kinetics of such reactions may be of importance.

Few authors have paid much attention to the kinetics of soil heavy metal reactions (as pointed out by Sparks (1985). In the Chapter 1, the influence of time on Cd and Cu uptake was discussed, but these tended to be experiments with a view towards pinpointing equilibrium positions, rather than investigating the stages leading up to such a state (Christensen (1984), Eriksson (1988)). Bunzl *et al* (1976) did so, but used conductivity changes as the means to that end. In doing so, they found that the kinetic order of affinity followed the thermodynamic order;

$$Pb > Cu > Cd \approx Zn > Ca.$$

But, when considering the half lives of these reactions, the order changed somewhat (principally due to the small amounts of some of the elements sorbed) to;

$$Ca > Zn \approx Cd > Pb > Cu,$$

the times in question being of the order of seconds.

Jopony and Young (1987) have attempted to study the kinetics of Cu^{2+} desorption using the Cupric ISE. Three kinetic equations were fitted, the only one where a mechanism can be implied from data fitting to the equation being a diffusion based equation;

$$C = K.\sqrt{t}$$

where K is a constant, t is the time

and C is concentration/activity.

The desorption could be fitted to all of the equations.

In a fixed time, batch approach, Brummer *et al* (1988) posited a two-step reaction, involving initial sorption followed by diffusion, of Ni, Zn and Cd using Goethite.

Hering and Morel (1989) mention that the complexation of trace metals by ligands is an intrinsically rapid process,

but go on to show that, if other ions are present, whilst $K_{stability}$ may imply a 'strong' reaction, retardation can occur, giving equilibration times in 10's of hours. Xue *et al* (1988) found that the uptake onto a biotic surface (Algae), whose surface molecules may be likened to those of soil organic material, indeed, Algae form part of the soils' microflora, followed the same uptake pattern described by Brummer *et al* (1988) - an initial very fast reaction, of surface sorption, followed by a longer period of uptake, which conformed to a diffusion equation. Bollag and Czaban (1989) have stressed the importance of bacteria in limiting Cd movement/uptake.

Stiff (1971) has clearly shown that the toxicity to fish of Cu is directly related to the amount of 'free' Cu^{2+} ion present in water (indeed, the presence of Cyanide reduces the toxic effect due to the complexation of the Cu). Minnich *et al* (1987) investigated the relationship between plant uptake and the Cu^{2+} activity: whilst no direct relationship was found, uptake was proportional to $(Cu^{2+})_{free}$. More importantly, Adams and Lund (1966) showed that free Al^{3+} was the causitive agent in the restriction of Cotton root growth. Clearly, the bioavailability of metals which have phytotoxic and environmental health implications associated with them need to be investigated, and the suggestion that a certain species (the 'free' metal) is a more potent form of the metal than any other should place the ISE firmly at the forefront of studies which attempt to monitor such ions, if electrodes are available.

In an attempt to define some of the areas in which ISE's may be employed in soils, the following series of experiments were set up:

(a). A pH static titration.

(b). A non-pH Static titration.

(c). A long term study.

(d). Kinetic observation.

5.2. Materials and Methods.

5.2.1. Procedural Outline.

In the first experiments, a soil suspension was titrated with Cd and Cu solutions, any fluctuations in pH being corrected by the addition of HNO_3 or NaOH. The second determination followed the same approach as the first, but in this instance the pH was allowed to range freely.

The long-term study looked at the changes in the cadmium and copper activity in suspensions over a period of approximately 1 month, whilst a very brief look at the uptake kinetics of one soil was examined.

5.2.2. Experimental.

The calibration and use of the electrodes follows the description in section 2.2.2.

(a). pH Static Titration.

A low and a high Cd and Cu concentration were selected for use in these titrations. The values chosen were limited by the availability of a cadmium salt (at the time), the absence of which required that a Spectrosol © (**BDH**) solution, for AAS work, was used to make up the Cd solutions, the pH's being matched to the equivalent Cu concentrations (Spectrosol © reagents are made up in $MHNO_3$) using MNaOH. Thus, the concentrations, made up in 0.1M $NaNO_3$, used were 0.267 mM and 4.45 mM Cd and Cu nitrate.

4.0g of air dry soil was suspended in 100mls. of 0.1M

$NaNO_3$ in a plastic beaker and allowed to come to equilibrium ie. when the pH remained invariant and the drift of the mV reading was below 0.1mV/min. Discrete portions of the low concentration Cd or Cu solution were added to the suspension via a 50.0ml. burette, until 50.0mls. of this solution had been added (or when the mV changes per addition became very small), at which point the titration was continued using the higher concentration solution. Following each addition, the pH was taken back to its original position (if any change had occurred) using 0.1 or 0.2M HNO_3 or NaOH. Activity readings were taken at 2 minutes following this correction (simply to standardise the procedure, as, particularly at low concentrations, the time taken to achieve $\leq$ 0.1mV/min. drift could be anything up to 60 minutes per addition). All 8 soils were used.

(b). Free Ranging pH.

The logistics of this experiment were very much the same as those in (a), with the exception that a single Cd and Cu concentration was used, and that no attempt was made to control the pH of the system. In addition to this, account was taken of the lower sensitivity of the Cd ISE, with respect to the Cu ISE, the Cd solution being 10^{-2}M $Cd(NO_3)_2$, whilst the Cu solution was 10^{-3}M $Cu(NO_3)_2$. Again, the soil:solution ratio was 1:25 (all 8 soils used), and the samples were pre-equilibrated in 0.1M $NaNO_3$ for 2 minutes. mV and pH readings were taken at 2 minute intervals.

(c). Long-Term.

Only 3 soils; Arkleston, Arkleston High Zinc and Fen Arable, were used in this experiment. 4.0g of air dry soil was suspended in 100mls. of 0.1M $NaNO_3$ at four Cd or Cu concentration levels (10, 40, 80 and 100μM): Four standards were also monitored for changes over time. The plastic bottles in which the suspensions were contained had been modified (by the addition of two extra holes) to enable pH and activity readings to be made *in-situ*. Following pH and mV measurement (2 minutes to equilibrate), the holes were sealed using **Nescofilm**, but the stoppers of the bottles were not fully tightened, to enable diffusion and permeation of gases in the systems. Measurements were taken at t_0, 24 hours, 1 week and progressively longer intervals. In the periods between measurements, the samples were kept at 25°C and shaken for 20 hours per week in an orbital shaker at 60rpm, which was sufficient to keep the slurry from sedimenting out.

(d). Kinetic Observations.

A variation on the titration approach was tried with one soil (Arkleston) to yield shorter term data, with a view to attempting some form of kinetic analysis.

A series of concentrations of both Cd and Cu (duplicated) were prepared in 0.1M $NaNO_3$ in 400ml plastic beakers;

Cd; 1.78, 3.56, 4.45, 8.90, 17.80, 35.60, 44.50, 89.00, 445.00, 890.00μM.

Cu; 2.00, 4.00, 8.00, 10.00, 20.00, 40.00, 100.00, 200.00, 1000.00, 2000.00μM.

When a stable electrode reading had been achieved in each of these solutions (100mls.), 4.0g of air dry soil was added, and readings were taken at 1 minute intervals until

the readings remained invariant or the change was ≤0.1 mV/min. The results were then subjected to various kinetic data manipulations;

$$0 \text{ order: } \partial C/\partial t = -k \text{ thus } C = -kt.$$

$$1^{st} \text{ order: } \partial C/\partial t = -kC \text{ thus } \ln C_0 - \ln C_t = kt.$$

$$2^{nd} \text{ order: } \partial C/\partial t = -k(C)^2 \text{ thus } 1/C_t - 1/C_0 = kt.$$

$$\text{Diffusion or Parabolic: } C = k\sqrt{t}.$$

C_0, C_t = initial and time 't' concentrations, t = time and k = rate constant.

5.3. Results.

(a). pH Static.

Once more it appears as though the Cd ISE results (shown in figure 5.1. a,b) will have to be discarded, as almost all of the experimental points lie above the line of the blank titration. One quite noticeable aspect of these experiments is especially clear at the lower end of the graphs. Lower pH soils are the ones which lie above the standard line (soil pH < 5.5), which suggests that the low soil pH is releasing ions which may interfere with the electrode. This trend extends to the higher concentrations too. Each titration took almost 1 hour to complete and there appeared to be very little difference between the standards and the samples, implying that the 'free-ion'-surface reaction is not a rapid one.

With the Cu titrations, as with the Cd ones, there are two distinct regions to the graphs, relating to the change in concentration of the titrant solution (figure 5.2. a,b). Examining the whole titration to begin with, the data points lie below the blank titration, which is as would be expected.

Figure 5.1. Cd pH Static ISE Titrations.

(a). Ark, AHZ, Cap and Dun.

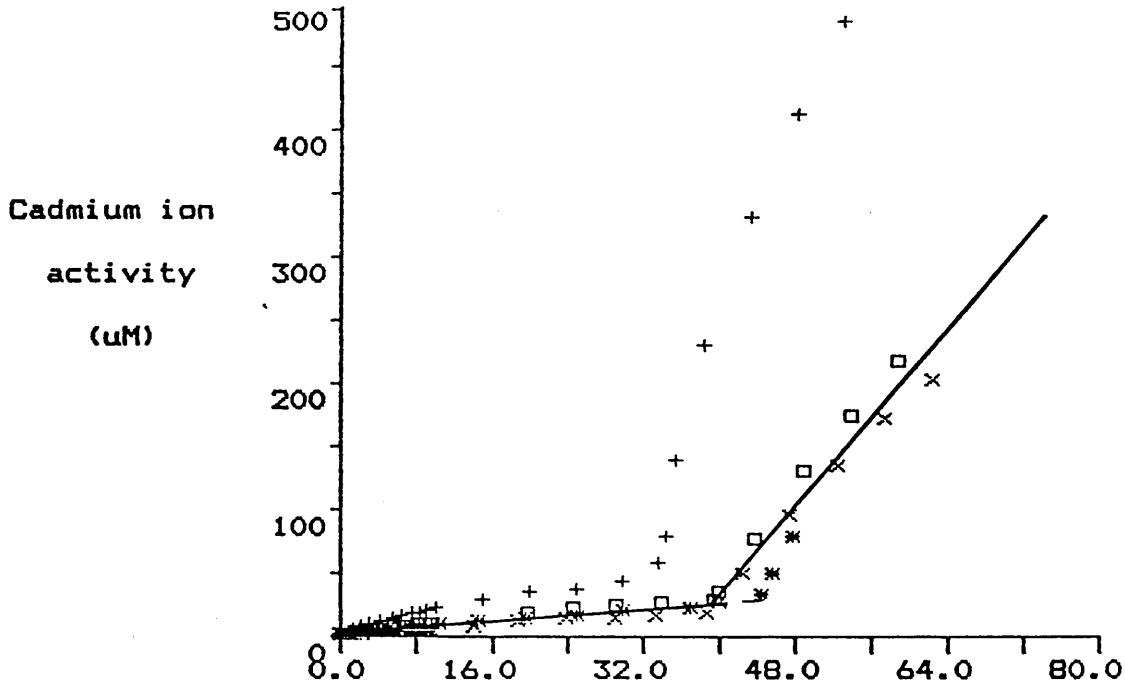
(b). BA, Dreg, FA and FS.

Figure 5.2. Cu pH Static ISE Titrations.

(a). Ark, AHZ, Cap and Dun.

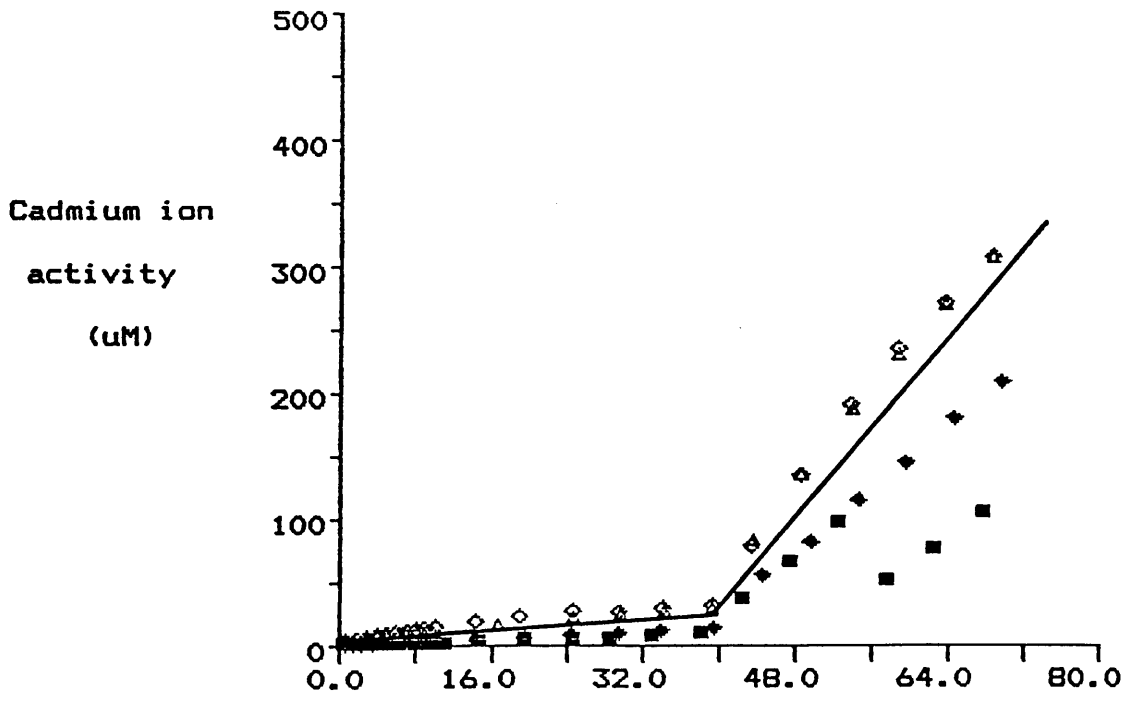
(b). BA, Dreg, FA and FS.

a



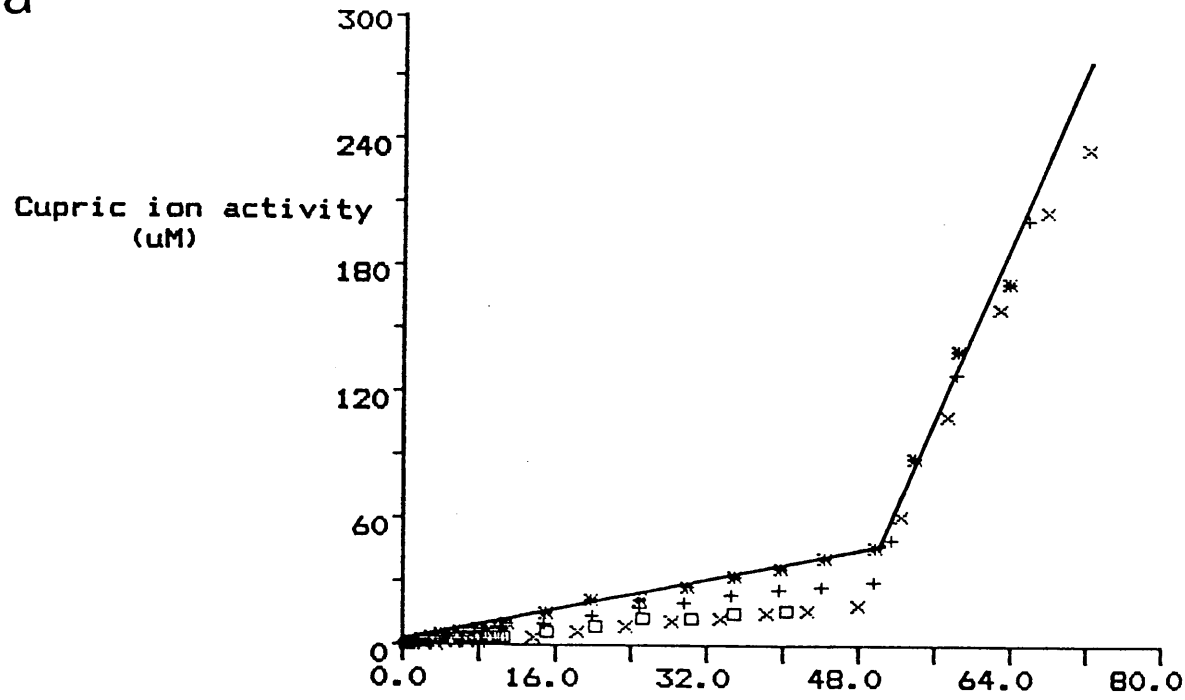
mls of a. 0.267 mM b. 4.45 mM Cd in 0.1M NaNO3 added.
(soil:solution = 1:25 VO = 100 mls)
ARKLESTON(pH 5.5) - * ARKLESTON HIGH ZINC(pH 4.9) - +
CAPRINGTON(pH 5.7) - x DUNLOP(pH 5.2) - sq.
pH STATIC ISE TITRATION.

b



mls of a. 0.267 mM b. 4.45 mM Cd in 0.1M NaNO3 added.
(soil:solution = 1:25 VO = 100 mls)
BLACKSTOUN(pH 5.3) - open dia. DREGHORN(pH 4.6) - open tri.
FEN ARABLE(pH 6.8) - sq. FEN SUBSOIL(pH 9.1) - dia.
pH STATIC ISE TITRATION.

a



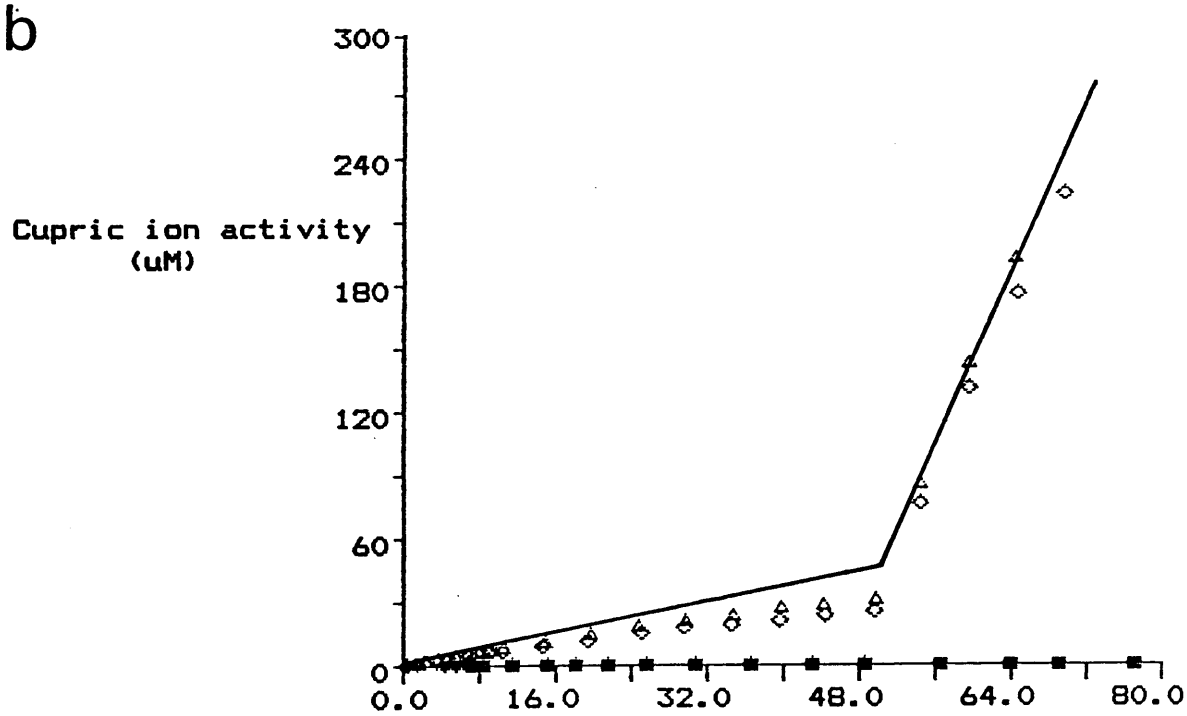
mls of a. 0.267 mM b. 4.45 mM Cu in 0.1M NaNO3 added.

(soil:solution = 1:25 VO = 100 mls)

ARKLESTON(pH 5.3) - * ARKLESTON HIGH ZINC(pH 4.8) - +

CAPRINGTON(pH 5.9) - x DUNLOP(pH 5.3) - sq.

b



mls of a. 0.267 mM b. 4.45 mM Cu in 0.1M NaNO3 added.

(soil:solution = 1:25 VO = 100mls).

BLACKSTOUN(pH 5.1) - open dia. DREGHORN(pH 4.7) - open tri.

FEN ARABLE(pH 8.7) - sq. FEN SUBSOIL(pH 8.3) - dia.

pH STATIC ISE TITRATION.

In the latter stages, the Ark, AHZ, Cap, Dun, BA and Dreg soils follow the blank titration very closely: Only the two Fen soils show deviation from this, maintaining $(Cu^{2+})_{free}$ levels well below the linear calibration range of the ISE for the whole procedure. At the lower end of the graphs, more differences appear; whilst BA and Dreg are almost linear, Cap progresses in a concave manner, becoming steeper as the titration proceeds . The remaining three 'acidic' soils have slight kinks in them at ≈6μM (Ark), ≈5μM (AHZ) and 4μM (Dun), whilst the two Fen soils lie on the x-axis.

Given that the titrations took place within the same time, an order of reaction can be drawn up;

FA ≈ FS > Cap > Dun > BA > Dreg > AHZ > Ark.

Decreasing rate of uptake.

This roughly corresponds to the order of decreasing pH and diminishing soluble organic matter.

(b). Free Ranging pH.

The graphs of this section are presented in figure 5.3. a-d.

In this experiment, the Cd ISE results appear to make more sense, in view of the fact that most of the data points lie below the standard titration - a far shorter equilibration time was used, compared to the previous set of experiments, each soil being stirred in its 0.1M $NaNO_3$ for only two minutes prior to the first metal addition and each titration lasting only ≈ 25 minutes. Still the results from two soils, AHZ and Dreg (two lowest pH's) results had to be rejected as they lay well above the line of the blank titration. The most striking feature was found in the FA, FS

and BA soils, where the increase in Cd activity is 'held back' in the initial stages, much in the manner of an S-shaped sorption isotherm. Ark shows this effect very slightly at low activities, and soon the activity of Cd in its presence begins to increase in an almost linear fashion, but with a steeper gradient than the blank titration. It appears as though, had the titration progressed, that the Ark line would have exceeded the blank line; this shows the time dependent nature of the interference with the electrode's operation.

The remaining two soils (Cap and Dun) display quite an erratic, undulating, response to the activity changes.

With the Cu systems, there is in almost all cases a gradual rise in the activity curve below the blank titration, again, bearing a strong similarity to the S-isotherm. The exceptions to this are the BA and the AHZ soils. The BA soil begins with this concave shape of the other graphs, but its gradient very rapidly increases, until it is well above the blank titration line. A similar situation is found with the AHZ soil - both soils curves decline again to a position below the blank curve. An intriguing feature of this behaviour is that the area under each graph matches the area under the blank graph, implying that no 'free' Cu^{2+} has been sorbed. The Dunlop soil shares some of this 'peaking' character, but stays below the blank line, whilst the Cap soil displays an incredible avidity in its removal of 'free' Cu^{2+} from solution.

The rapidity of uptake for Cd and Cu can be summarized as follows;

Cd; BA > Ark > FA ≈ FS > Dun > Cap.

Cu; Cap > FS > FA > Ark > Dreg > Dun > AHZ ≈ BA.

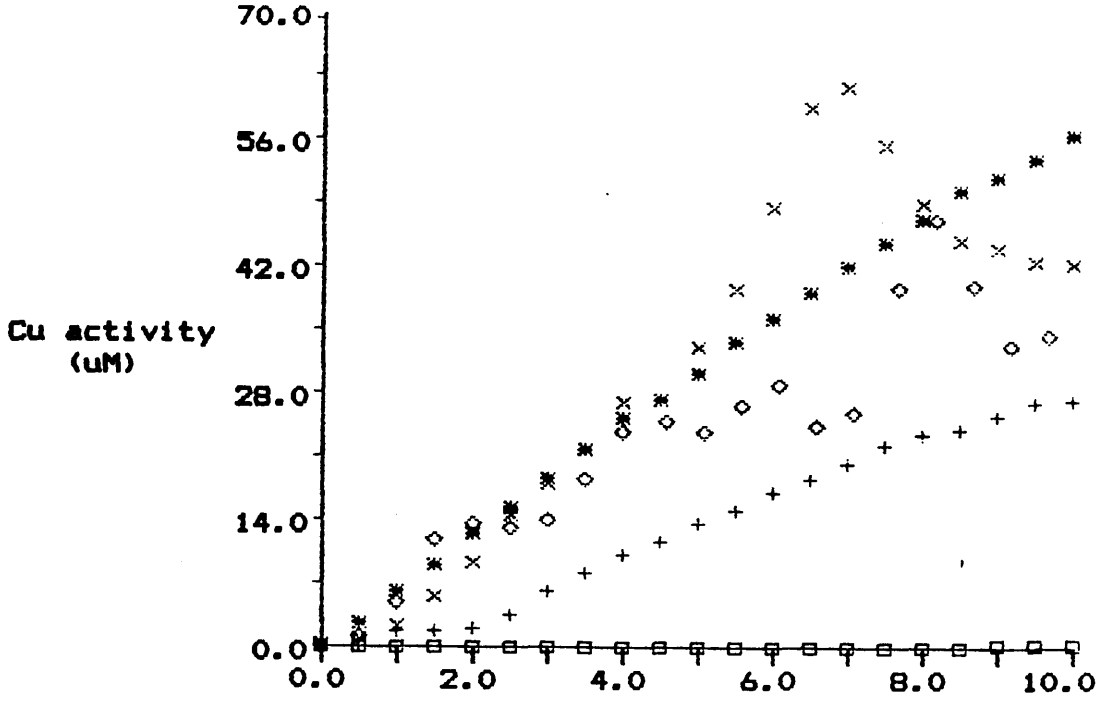
The pH changes encountered in this experiment, and those expected on account of the titrant alone are detailed in

table 5.1.

Figure 5.3. Cu and Cd Free Ranging pH ISE Titrations.

Figure 5.3 Cu and Cd Free Ranging pH ISE Titrations;
(a) and (b). Copper.
(c) and (d). Cadmium.

a



mls of M/10^3 Copper in 0.1M NaNO3 added.

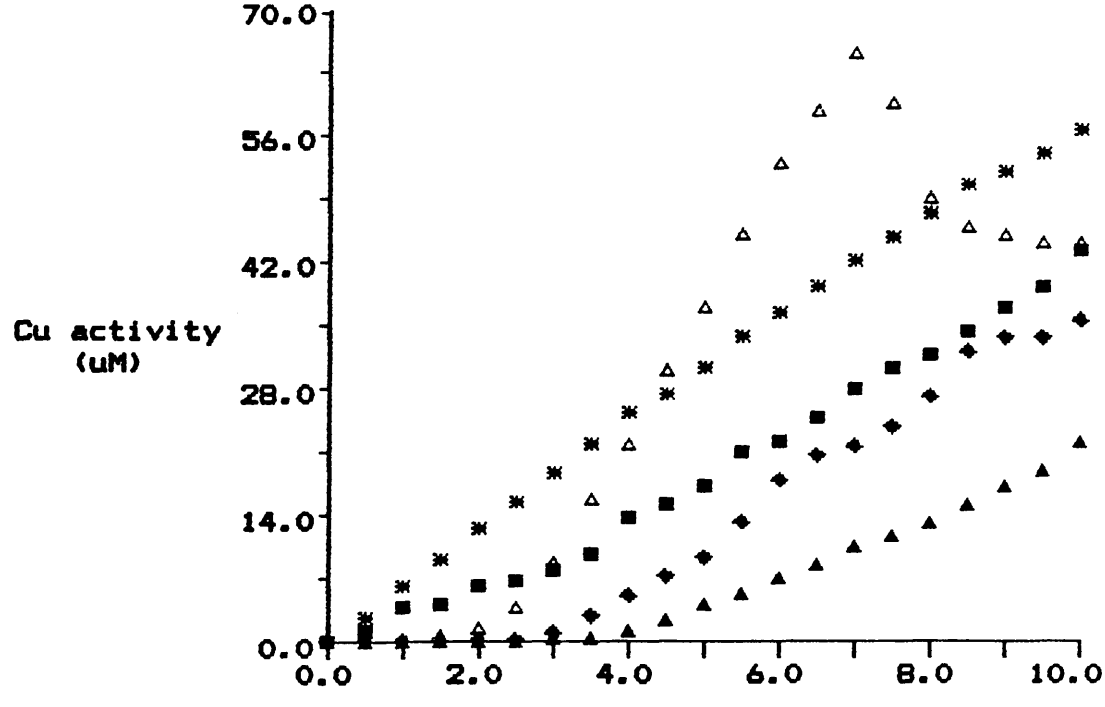
Copper ISE titration, free ranging pH.

Blank - * Arkleston - + Arkleston High Zinc - x

Caprington - sq. Dunlop - dia.

(soil:solution = 1:25 V0 = 50 mls Vf = 60 mls).

b



mls of M/10^3 Copper in 0.1M NaNO3 added.

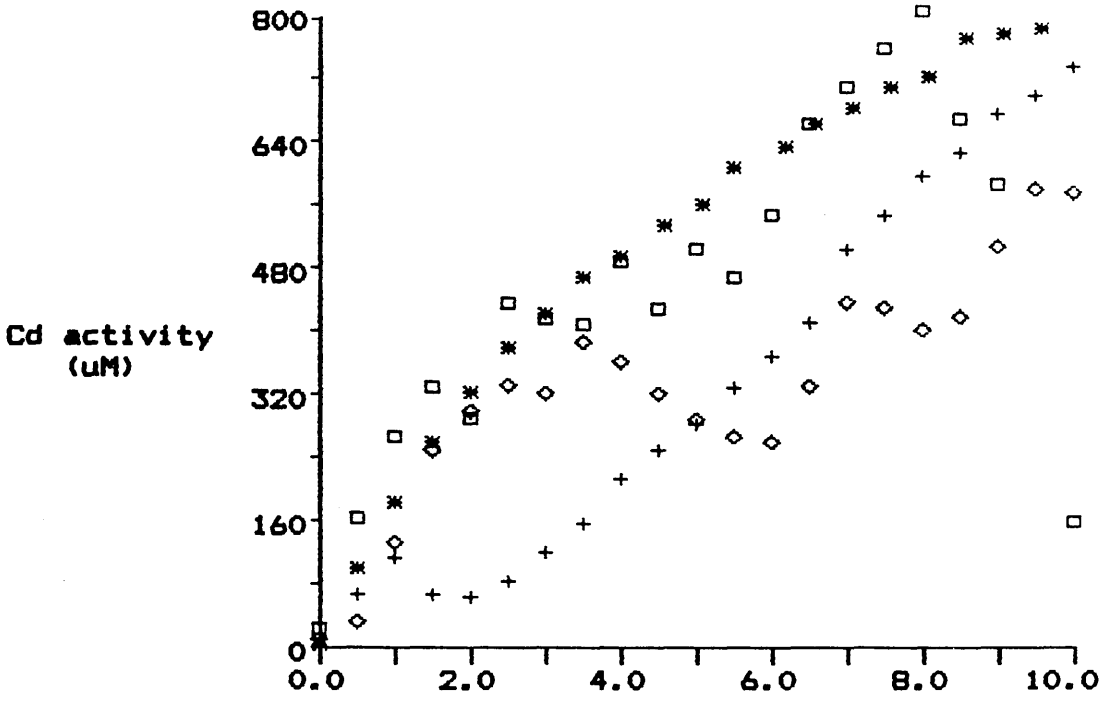
Copper ISE titration, free ranging pH.

Blank - * Blackstoun - open tri. Dreghorn - sq.

Fen Arable - dia. Fen Subsoil - tri.

(soil:solution = 1:25 V0 = 50 mls Vf = 60 mls).

c



mls of M/10^2 Cadmium in 0.1M NaNO3 added.

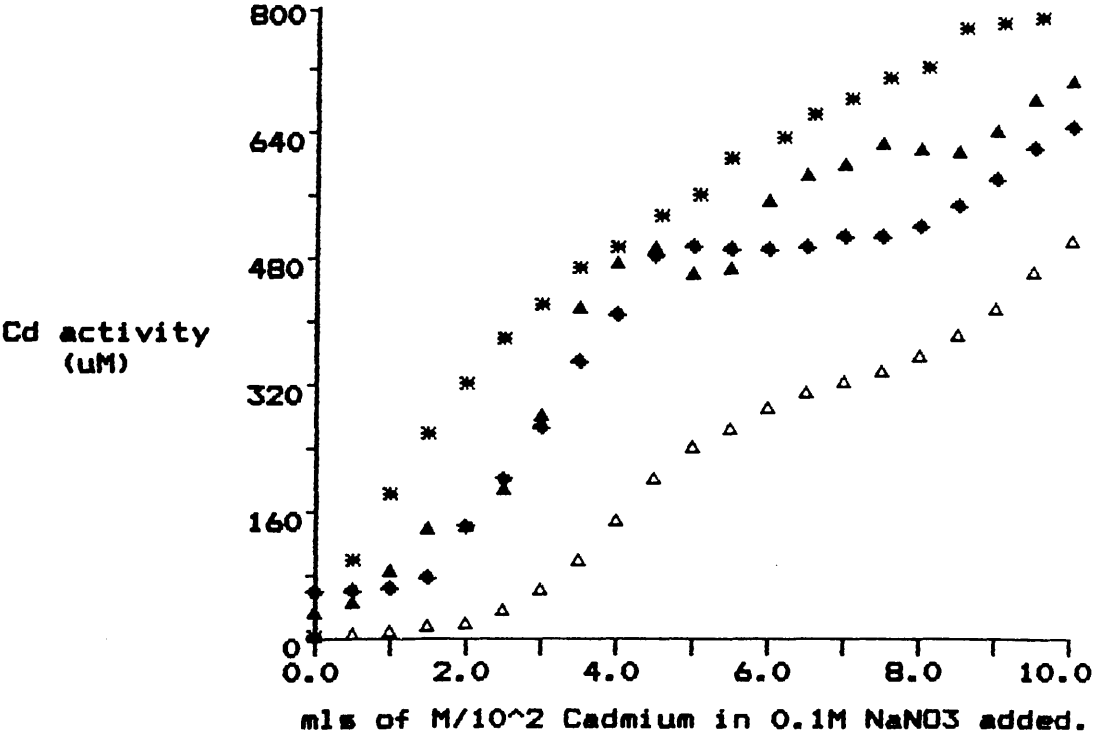
Cadmium ISE titration, free ranging pH.

Blank - * Arkleston - x Caprington - open sq.

Dunlop - open dia.

(soil:solution = 1:25 V0 = 50 mls Vf = 60 mls).

d



mls of M/10^2 Cadmium in 0.1M NaNO3 added.

Cadmium ISE titration, free ranging pH.

Blank - * Blackstoun - open tri.

Fen Arable - dia. Fen Subsoil - tri.

(soil:solution = 1:25 V0 = 50 mls Vf = 60 mls).

Table 5.1. Free Ranging pH Changes.

Soil	Initial pH	Eq. Actual pH	Expected pH*
		Cd	
Ark	5.58	5.46	5.46
Cap	5.94	5.82	5.68
Dun	5.28	5.18	5.26
BA	5.58	5.38	5.48
FA	6.96	6.76	5.91
FS	8.54	7.86	5.94
		Cu	
Ark	5.58	4.98	4.82
AHZ	5.14	4.58	4.72
Cap	5.68	5.78	4.83
Dun	5.22	4.96	4.74
BA	5.36	4.88	4.78
Dreg	4.74	4.48	4.55
FA	6.66	5.30	4.88
FS	9.12	6.52	4.88

* based on blank titration pH change.

Cd - 6.86×10^{-8} moles of protons 'added'.

Cu - 7.87×10^{-7} moles of protons 'added'.

(c). Long Term.

The graphs of this data are presented in figure 5.4. (a-f).

The AHZ measurements for the long term Cd experiment had to be discarded as, even after 24 hours, the suspension Cd readings were far higher than the standards. The Ark measurements, in this instance, appeared to be more

acceptable than those found in the fixed pH experiment. Certainly, it and the FA soil gave reasonable results up until 14 days, both showing a rapid initial decrease, continuing up to 24 hours. The next measurement, however showed that the activities were climbing again, the last Ark measurements being higher than the standards at this stage, which had shown a drop, followed by a resumption of their initial readings, followed in turn by a very sharp drop at day 30.

Figure 5.4. (d-f) shows the Cu results, which display the expected pattern of a sharp decrease followed by a longer term, less rapid, drop in activity (the FA results are not shown as, even at the instantaneous first measurement, the levels of $(Cu^{2+})_{free}$ were well below the linear calibration range of the electrode). Unlike the Cd standards, the Cu ones showed very little variation with time. The uptake range may be summarized;

Cu; FA > Ark > AHZ.

——————————>

Decreasing rate of uptake.

The only comment-worthy trend in Cu pH was the gradual rise of the FA system pH, also found in the Cd experiments, that being almost 1.0 pH unit.

Figure 5.4. Long-Term ISE Measurements;

(a). Ark-Cd.

(b). FA-Cd.

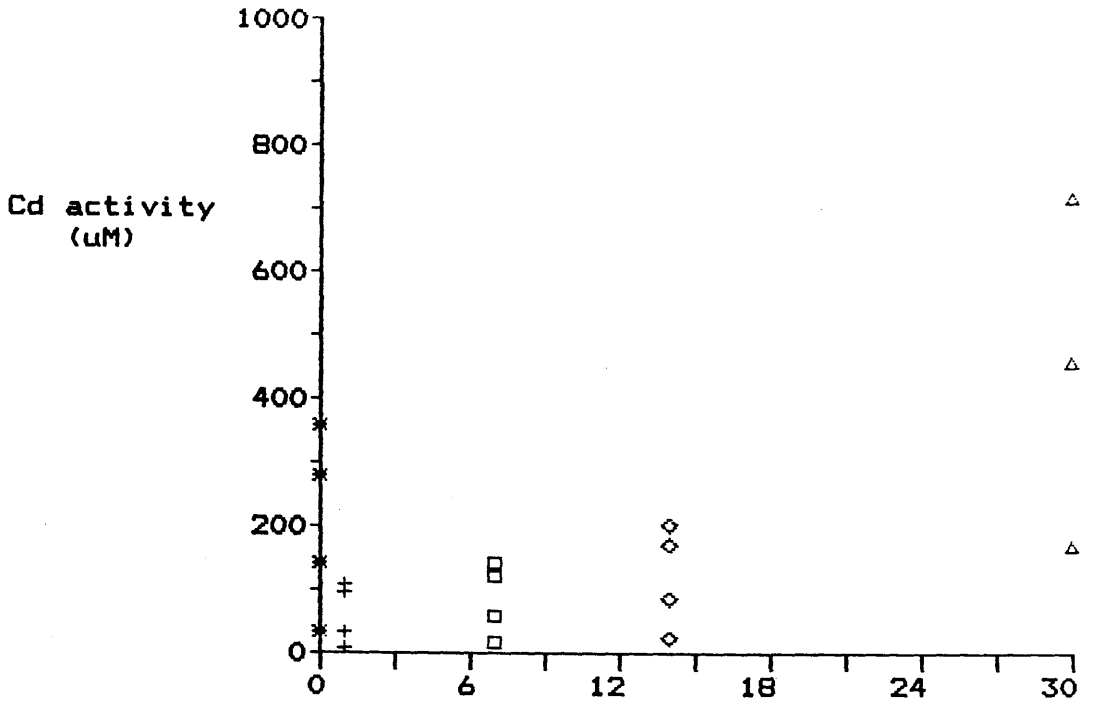
(c). Standards-Cd.

(d). Ark-Cu.

(e). AHZ-Cu.

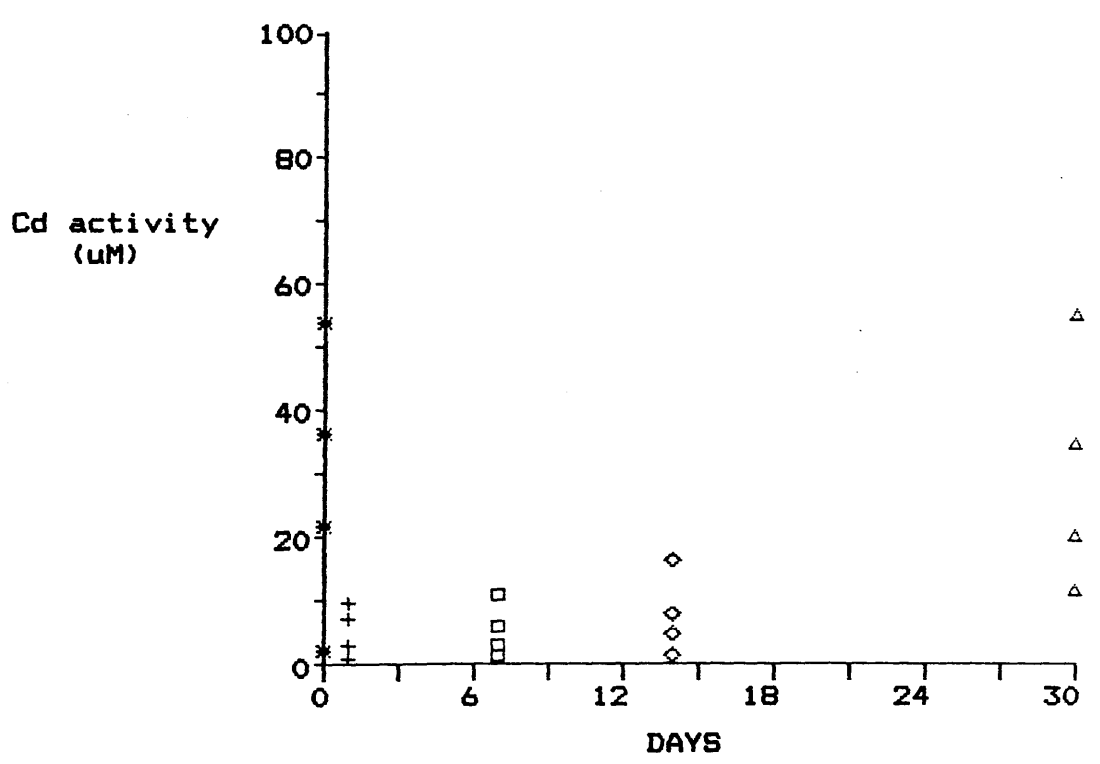
(f)..Standards-Cu.

a



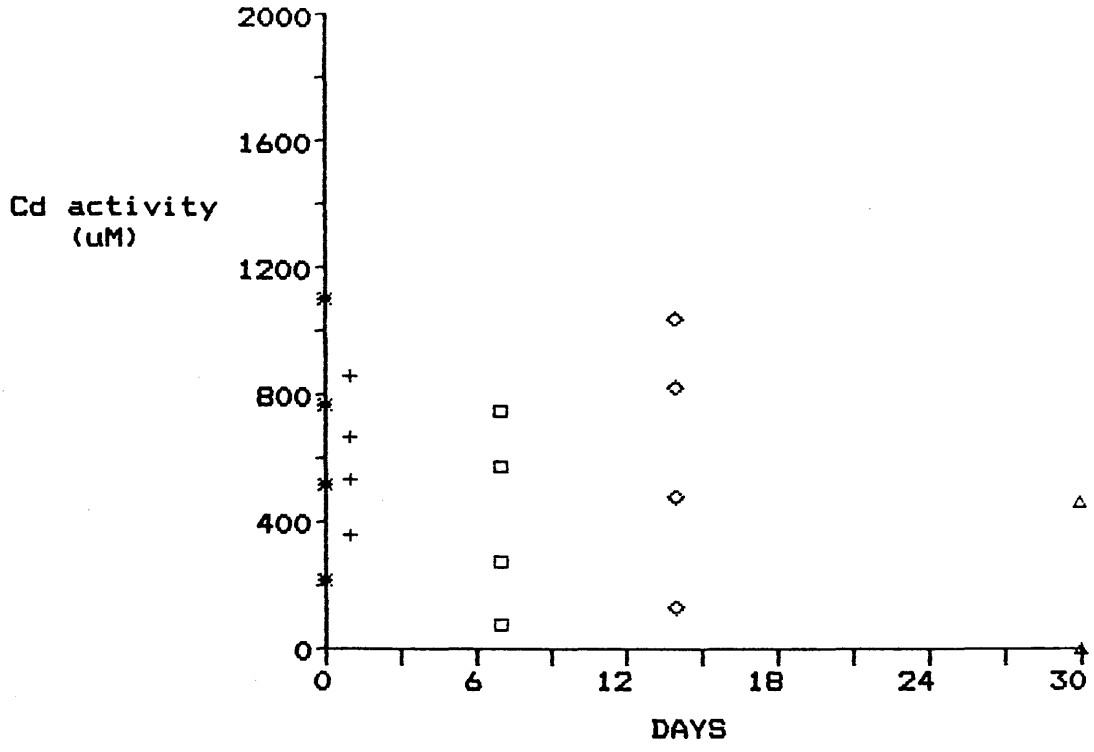
Long term Cd ISE measurements.
ARKLESTON.

b



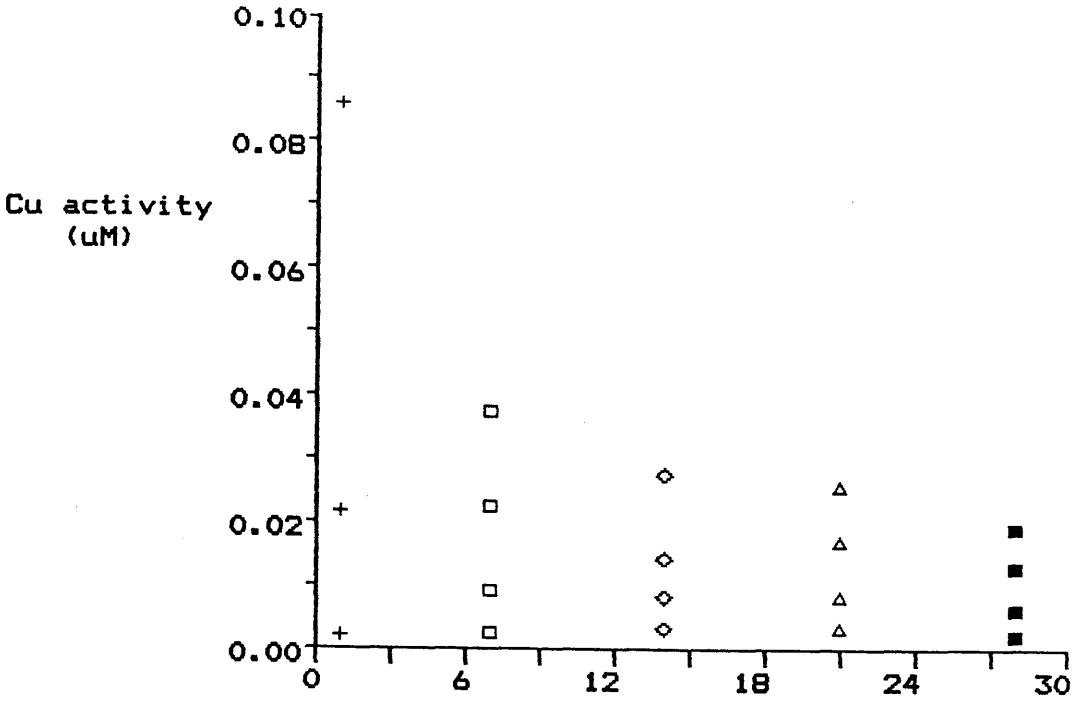
Long term Cd ISE measurements.
FEN ARABLE.

C



Long term Cd ISE measurements.
STANDARDS.

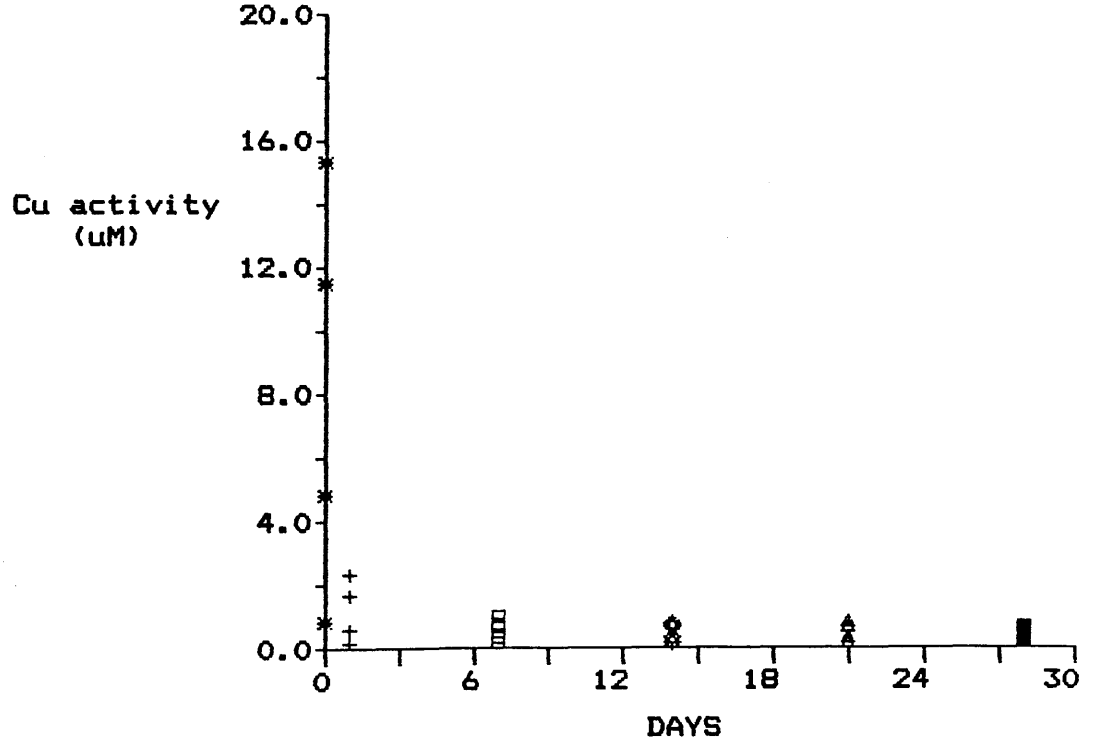
d



Long term Cu ISE measurements.

ARKLESTON

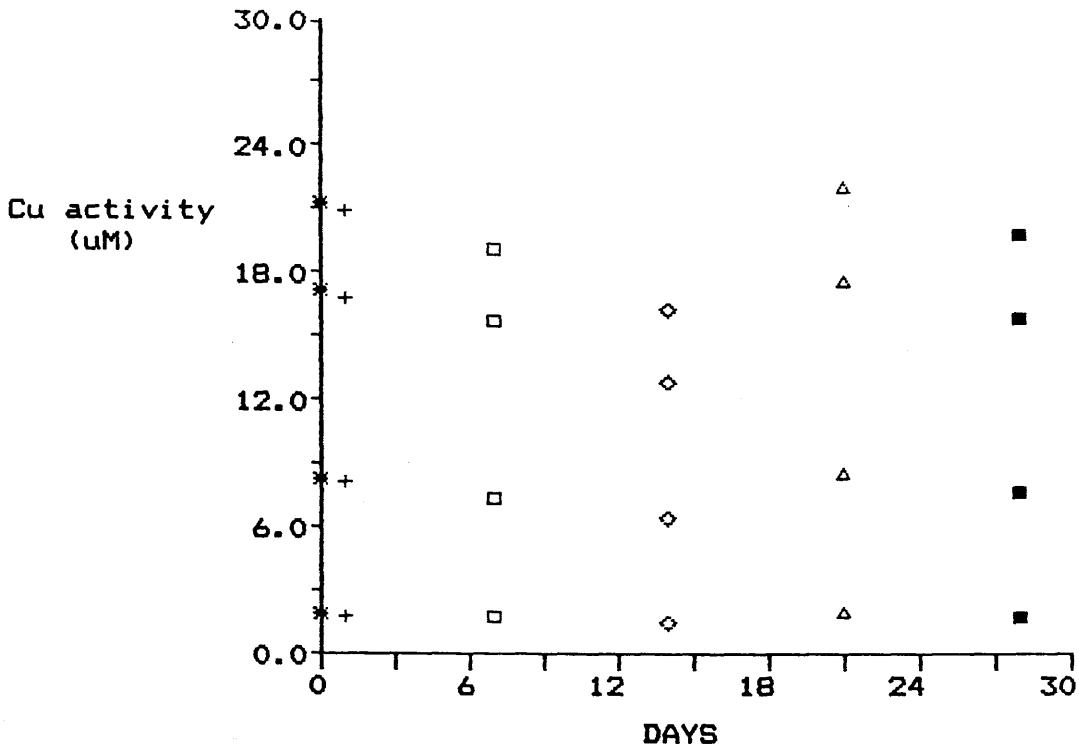
e



Long term Cu ISE measurements.

ARKLESTON HIGH ZINC.

f



Long term Cu ISE measurements.

STANDARDS.

(d). Kinetic Observations.

The duplicate graphs of the 1.78 and 10μM levels are shown in figure 5.5. (a and b) for Cd and Cu.

The Cd points reproduce to a higher degree than the Cu ones, and equilibrium is achieved within ≈ 4 minutes for the the Cd system and ≈ 6 minutes for the Cu system. All the other concentrations displayed this behaviour, except at the very highest levels, where adding in the soil made little impact on the ion activity within the duration of the experiment. The initial rapid stage of the uptake/partitioning could not be described by any of the previously listed equations, but the latter stages could be described almost equally well by the 4 equations (r^2 > 0.990).

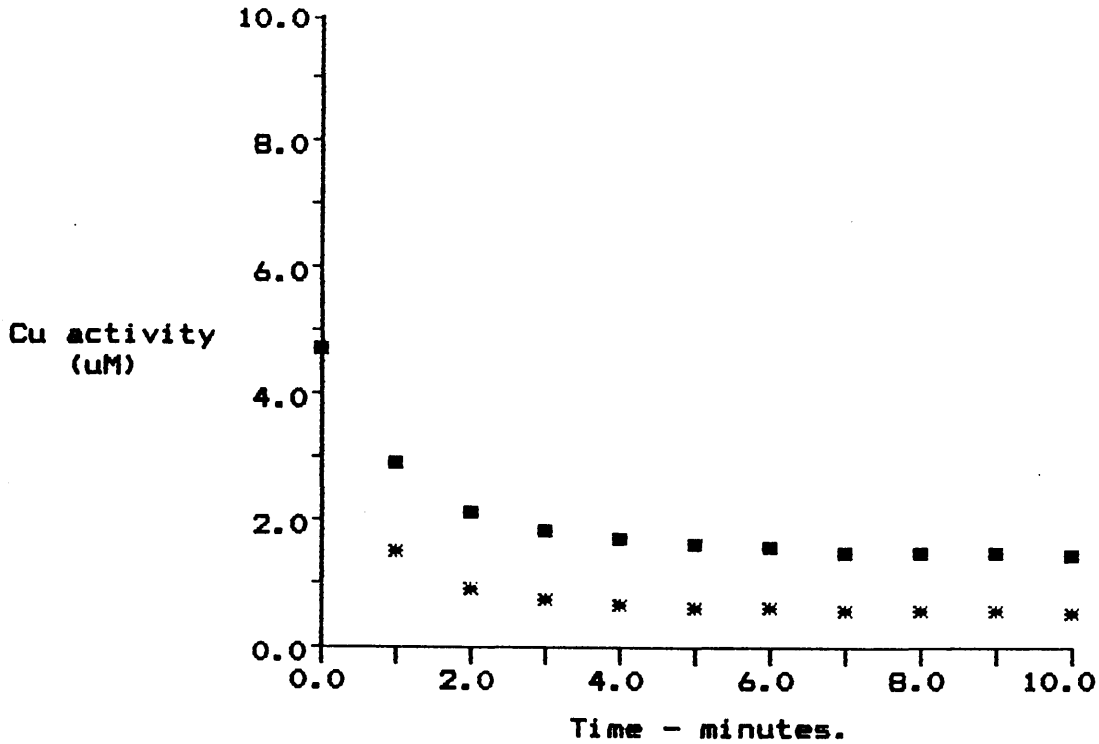
Figure 5.5. Short-Term Kinetic Observations on Free Cd and Cu in solution.

Figure 5.5. Short-Term Kinetic Observations on Free Cd and Cu in solution;

(a). Cu - $[Cu]_{total}$ = 10μM.

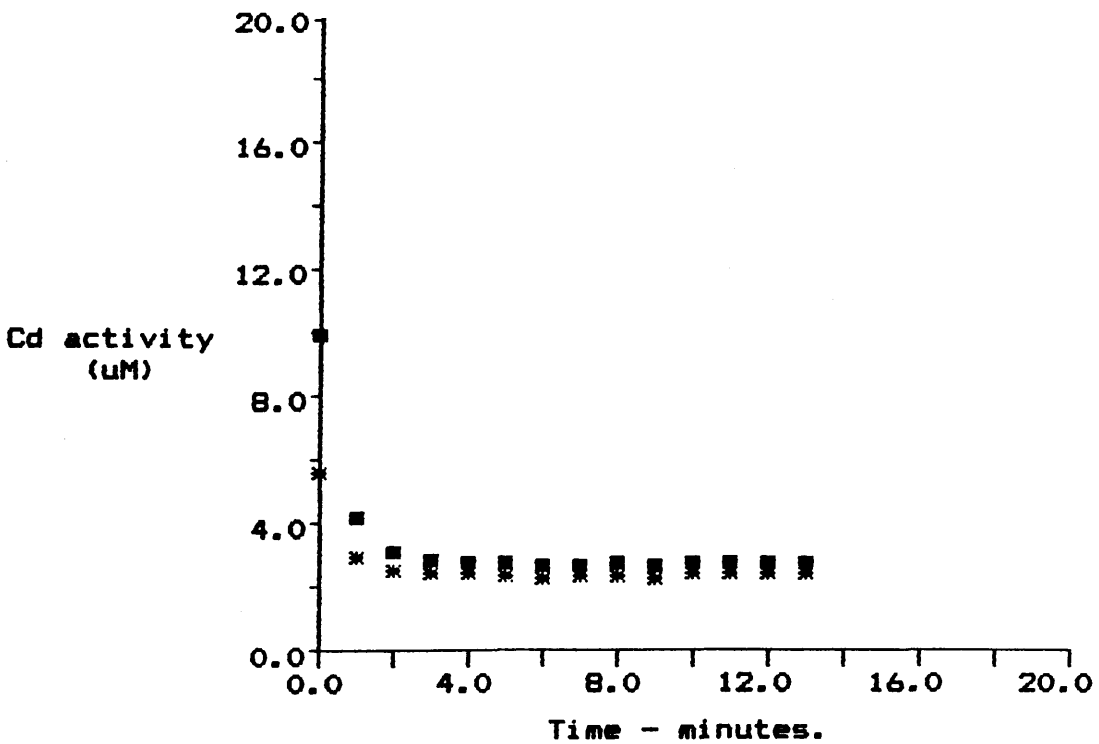
(b). Cd - $[Cd]_{total}$ = 2μM.

a



Change in ISE reading with time, in presence of soil.
Arkleston - soil:solution = 1:25.

b



Change in ISE reading with time, in presence of soil.
Arkleston - soil:solution ratio = 1:25.

5.4. Discussion.

The influence of acidic soil cations (Al^{3+}) on the Cd ISE has been noted by Cavallaro and McBride (1980b), and given the limitations communicated by the manufacturers (section 2.2.2.), it would seem that the Cd ISE is inappropriate for any study which includes soils and has a duration of more than 30 minutes. This is very unfortunate, as the speciation of Cd is of great environmental importance. In only two experiments does it seem that the Cd ISE figures could be believed - the free ranging pH and the uptake kinetics investigation.

Tills and Alloway (1983) proposed a scheme by which to speciate Cd and noted that the Cd ISE could not be used in their scheme, owing to interference which they ascribed to Cu^{2+} ions. A further point of interest regarding the use of ISE's in soil studies is that, as commented upon earlier, few studies are being carried out using them as analytical tools; Sanders (1982) advocated their use, but more recently Sanders and McGrath (1988) resorted to using calculative based methods when looking at copper complex formation.

With the Arkleston soil the pH static experiment and the kinetics experiment results showed good agreement - at high levels changes in activity with time were undetectable, and, given that most of the other soils mimic this behaviour, we could reasonably extrapolate a similar set of reaction kinetics to describe the uptake of Cu to the other soils.

Some discrepancy, however did appear at the low end of the activity scale - the results of the pH static titration followed the standard graph quite closely, whilst the kinetic examination showed quite a marked decrease in activity when the soil was added. If we look at the free

ranging pH results, a similar drop below the standard description is observed, implying that in the pH static experiment, the congruence of the standards and the samples was due to the pH control.

The sorption kinetics are certainly in agreement with the findings of other authors; Bunzl *et al* (1976), Jopony and Young (1987), Brummer *et al* (1988) and Xue *et al* (1988), where (interpolating from the Ark kinetic assessment) there is an initial very rapid uptake followed by a much slower, gradual removal, both on a macro- (long term) and a microscopic scale. However, the data obtained fails to conform with any great conviction to any of the 4 equations to which the data was applied.

Perhaps the most intriguing aspect of performing what are essentially sorption isotherms in this way is the difference with respect to the batch-concentration isotherms.

Where pH control is maintained, the sequence of uptake conforms to that found in the first series of Cu sorption isotherms, whereas the low level selectivity sequence is very different - this suggests that at high concentrations, Cu uptake can certainly be related to the total Cu presence, whilst at low concentrations other species may be challenging $(Cu^{2+})_{free}$ in terms of relative uptake importance.

The free ranging pH sequence is different again. In light of the way in which the additions tend to depress the solution pH (table 5.1.), whilst solutions of equivalent concentration will tend to, in batch experiments, equilibrate to the pH of the 0.1M NaNO3 suspension, the short term differences in the free ranging set of isotherms may be due to this ephemeral pH change. From this it can be

said that where the contact time of a solution with a soil surface is short, the solution pH be important in terms of the solution components reaction with the soil.

The sorption isotherms of Chapter 3, when measured with the Cu ISE, displayed S-character , with the FA and BA soils. This is borne out in the free ranging titrations, despite the pH drop brought about by the titration. Whilst Neal and Sposito (1986) had demonstrated such a sorption curve for Cd, this effect was absent in the isotherms shown in Chapter 3, but in the free ranging pH experiments, there is a pronounced 'sluggishness' in the removal of $(Cd^{2+})_{free}$ from solution in 3 (FA, FS and Cap) soils where we would expect to see an organic effect. Given that the pH falls in these experiments, it may be stated that the metal ions are being taken up into forms kinetically stable with respect to protons.

Certainly, in the free ranging pH tests, the expected drop in pH is greater than the actual pH drop, suggesting that the soil is buffering the pH changes by sorbing, or exchanging cations with, H+, even in this short term, so perhaps the alterations to the soluble organic matter component of the solution lie at a greater time interval than this: Hering and Morel (1989) have observed that speciation changes need not occur rapidly in solution. The virtual absence of the S-shape isotherm from the pH static titrations implies that the added HO^- is retarding the formation of the soil solution-organic complexes, with the exception of the Caprington soil, which had previously demonstrated a very great capacity for Cu^{2+} removal from solution.

5.5. Overview of Chapter 5.

There are very many parameters to control in soil experiments, such as to make disentangling specific effects from data a major task: Thus, when pH changes, soluble organic matter levels change and hydroxy-species distribution changes. If I is altered, surface charge alters, solution pH alters and electrical double layers may expand or compress.

Given that the sample titrations performed in the controlled pH experiment follow the standard ones so closely, it is tempting to conclude that the observed uptake is due to the existence of species other than $(Cu^{2+})_{free}$. However, at pH 7, 53% of the Cu is present as the free ionic form, and for soils below this pH, uptake is certainly (from the Chapter 3 figures) greater than 47% of that added. For this reason this concept must be rejected. *

In performing titrimetric determinations, unless very low volumes of very high concentration solutions are used, soil:solution ratios change and remove one of the few variables over which we have definite control. Thus, we are limited in the interpretation of the results to a largely comparitive approach.

* (bearing in mind that the system is in a dynamic equilibrium).

Points to note:

(a). Low pH soils react more slowly (Where Rate = $\Delta(Cu^{2+})$/vol. added) than high pH soils.

(b). Soluble organic materials reduce this rate of change for both Cd and Cu.

(c). HO^- can reduce the metal ion-organic matter interaction, in the short term.

(d). Short-term drops in pH little influence the organic matter-metal interaction.

(e). Long-term changes in $(Cu^{2+})_{free}$ occur with minimal pH change.

(f). Soils of low exchangeable base status will be much influenced by the contact time and the solution pH.

Appendix 1. Speciation Equations and BBC Basic Programs for Carrying out Speciation Calculations.

Appendix 1: Speciation Equations.

All constants are taken from Lindsay (1979) and Perrin (1979).

(a). pCO_2 is taken as $10^{-3.52}$ Atm.

(b). I = 0.1, therefore, according to the Davies equation; $\log ¥ = -A.z^2.\left((\sqrt{I}/(1+\sqrt{I})) - 0.3.I\right)$

where ¥ is the activity coefficient, I is the ionic strength, z is the valence of the ion in question and A is a constant.

$¥_{+,-} = 0.781$ $¥_{2+,2-} = 0.372$ $¥_{3+,3-} = 0.108$.

(c). The stability constants chosen are all in terms of activity, thus, where major solution components are used (ie $[NO_3^-]$, they are multiplied by the appropriate activity coefficient.

(d). In the Citrate speciation programme, to enable a solution to be found to the equation, it is assumed that the influence of Cd and Cu complexation upon the amount of Citrate ligands is minimal. Using this assumption we can, via the total Citrate concentration, solve an equation for a Citrate species activity, which can be inserted into the metal speciation calculation.

(e). Only certain species are considered: the free, hydroxy, background electrolyte and Carbonate forms.

Cd in 0.1M $NaNO_3$

$$[Cd^{2+}]_{total} = (Cd^{2+})_{free} \left\{ 1/\text{¥}_{2+} + 10^{pH-9.99} + 10^{2pH-20.3} + 10^{pH-9.14} + 10^{2pH-17.58} + 0.204 + 1.644 \times 10^{-2} \right\}$$

Cu in 0.1M $NaNO_3$

$$[Cu^{2+}]_{total} = (Cu^{2+})_{free} \left\{ 1/\text{¥}_{2+} + 10^{pH-7.59} + 10^{2pH-13.78} + 10^{pH-9.14} + 10^{2pH-14.95} + 0.316 + 2.43 \times 10^{-3} \right\}$$

Cd in 0.1M NaCl

$$[Cd^{2+}]_{total} = (Cd^{2+})_{free} \left\{ 1/\text{¥}_{2+} + 10^{pH-9.99} + 10^{2pH-20.3} + 10^{pH-9.14} + 10^{2pH-17.58} + 9.55 + 2.43 + 0.15 + 10^{-4} \right\}$$

Cu in 0.1M NaCl

$$[Cu^{2+}]_{total} = (Cu^{2+})_{free} \left\{ 1/\text{¥}_{2+} + 10^{pH-7.59} + 10^{2pH-13.78} + 10^{pH-9.14} + 10^{2pH-14.95} + 0.25 + 4.63 \times 10^{-3} \right\}$$

Cd in 0.033M Na_2SO_4

$$[Cd^{2+}]_{total} = (Cd^{2+})_{free} \left\{ 1/\text{¥}_{2+} + 10^{pH-9.99} + 10^{2pH-20.3} + 10^{pH-9.14} + 10^{2pH-17.58} + 3.49 \right\}$$

Cu in 0.033M Na_2SO_4

$$[Cu^{2+}]_{total} = (Cu^{2+})_{free} \left\{ 1/\text{¥}_{2+} + 10^{pH-7.59} + 10^{2pH-13.78} + 10^{pH-9.14} + 10^{2pH-14.95} + 2.84 \right\}$$

Cd in 0.0167M $Na_3Citrate$

$$[Cd^{2+}]_{total} = (Cd^{2+})_{free} \left\{ 1/¥_{2+} + 10^{pH-9.99} + 10^{2pH-20.3} + 10^{pH-9.14} + 10^{2pH-17.58} + 10^{1.08}(H_2L^-) + 10^{pH-2.15}(H_2L^-) + 10^{2pH-5.39}(H_2L^-) \right\}$$

Cu in 0.0167M $Na_3Citrate$

$$[Cu^{2+}]_{total} = (Cu^{2+})_{free} \left\{ 1/¥_{2+} + 10^{pH-7.59} + 10^{2pH-13.78} + 10^{pH-9.14} + 10^{2pH-14.95} + 10^{2.37}(H_2L^-) + 10^{pH-0.93}(H_2L^-) + 10^{2pH-4.03}(H_2L^-) \right\}$$

The procedure for speciating Cd and Cu in 0.0167M $Na_3Citrate$ assumes that the $\partial[Citrate]_{total}$ on complexation of Cd^{2+} or Cu^{2+} is so small as to be insignificant: such an assumption is tolerable up to $\approx 10^{-4}M$ M^{2+} at least. ie.

50mls of 0.0167M Citrate = $10^{-3.08}$ moles of Citrate

50mls of $10^{-4}M$ M^{2+} = $10^{-5.30}$ moles of M^{2+}

If all of this metal were involved in a 1:1 complex, irrespective of its speciation, then the amount of un-combined Citrate would be;

$$(10^{-3.08} - 10^{-5.30}) \times 10^{5.08} = 99.4\%$$

Given this high 'residual' Citrate, the assumption proposed is validated and the speciation equations may be solved.

Solving the Citrate Equation.

We can say that the total Citrate concentration is equal to the sum of its species;

$$[Cit]_{total} = \left\{(CitH_3^{\circ}) + (CitH_2^{-})/¥_{-} + (CitH^{2-})/¥_{2-} + (Cit^{3-})/¥_{3-} + (Cu(Cit)^{-})/¥_{-} + (Cu(CitH)^{\circ}) + (Cu(CitH_2)^{+})/¥_{+}\right\}$$

Which can be rearranged to the form;

$$[Cit]_{total} = (H_2L^{-})_{free}\left\{1/¥_{-} + 10^{2.87-pH} + 10^{pH-3.92} + 10^{pH-9.07} + 10^{2.37}(Cu^{2+})_{free} + 10^{pH-0.93}(Cu^{2+})_{free} + 10^{2pH-4.03}(Cu^{2+})_{free}\right\}$$

In the light of the previous assumptions, we can omit the terms involving Copper from this equation, thus to arrive at a value of (H_2L^{-}) to insert into the Cu speciation calculation.

```
*EXEC CUNO3
.LET K1=1/0.372
 RESULT=2.68817204
.LET K2=0.316
 RESULT=0.316
.LET K3=2.43*10^-3
 RESULT=2.43E-3
.LET C3=10^(C2-7.593)
.LET C4=10^((C2*2)-13.78)
.LET C5=10^(C2-9.143)
.LET C6=10^((C2*2)-14.95)
.LET C7=1/(K1+K2+K3+C3+C4+C5+C6)
.LET C8=C7*C1
.LET C9=C7*K1
.NAME C9 '%Cu'
.LET C10=C7*C3
.NAME C10 '%HO1'
.LET C11=C7*C4
.NAME C11 '%HO2'
.LET C12=C7*C5
.NAME C12 '%HCO3'
.LET C13=C7*C6
.NAME C13 '%CO3'
.LET C14=C7*K2
.NAME C14 '%NO3'
.LET C15=C7*K3
.NAME C15 '%(NO3)2'
```

```
    EXEC CUSO4
.LET C3=10^(C2-7.59)
.LET C4=10^((C2*2)-13.78)
.LET C5=10^(C2-9.14)
.LET C6=10^((C2*2)-14.95)
.LET K1=1/0.372
 RESULT=2.68817204
.LET K2=2.84
 RESULT=2.84
.LET C7=1/(C3+C4+C5+C6+K1+K2)
.LET C8=C1*C7
.LET C9=C7*K1
.LET C10=C7*C3
.LET C11=C7*C4
.LET C12=C7*C5
.LET C13=C7*C6
.LET C14=C7*K2
.NAME C1 '(Cu)'
.NAME C2 'pH'
.NAME C8 'Cu act'
.NAME C9 '%Cu'
.NAME C10 '%HO1'
.NAME C11 '%HO2'
.NAME C12 'HCO3'
.NAME C13 'CO3'
.NAME C14 'SO4'
```

```
*EXEC CUCL
.LET K1=1/0.372
 RESULT=2.68817204
.LET K2=0.25
 RESULT=0.25
.LET K3=4.627*10^-3
 RESULT=4.627E-3
.LET C3=10^(C2-7.59)
.LET C4=10^((2*C2)-13.78)
.LET C5=10^(C2-9.14)
.LET C6=10^((2*C2)-14.95)
.LET C7=1/(K1+K2+K3+C3+C4+C5+C6)
.LET C8=C1*C7
.LET C9=C7*K1
.LET C10=C7*C3
.LET C11=C7*C4
.LET C12=C7*C5
.LET C13=C7*C6
.LET C14=C7*K2
.LET C15=C7*K3
.NAME C1 'Cu tot' C3 'pH' C8 'Cu act' C9 '%Cu' C10 '%HO1' C11 '%HO2' C12 '%HCO3'
C13 '%CO3' C14 'CuCl' C15 'CuCl2'
```

```
*EXEC CUCIT
.LET C4=C3/((10^(2.87-C2))+1.28+(10^(C2-3.92))+(10^((C2*2)-11.01)))
.LET C5=10^(C2-7.59)
.LET C6=10^((C2*2)-13.78)
.LET C7=10^(C2-9.14)
.LET C8=10^((C2*2)-14.95)
.LET C9=(10^2.37)*C4
.LET C10=(10^(C2-0.93))*C4
.LET C11=(10^((C2*2)-4.03))*C4
.LET K1=1/0.372
 RESULT=2.68817204
.LET C12=1/(K1+C11+C10+C9+C8+C7+C6+C5)
    .LET C13=C12*C1                .NAME C15 '%H01'
    .LET C14=C12*K1                .NAME C16 '%H02'
    .LET C15=C12*C5                .NAME C17 '%HCO3'
    .LET C16=C12*C6                .NAME C18 '%CO3'
    .LET C17=C12*C7                .NAME C19 '%H2L'
    .LET C18=C12*C8                .NAME C20 '%HL'
    .LET C19=C12*C9                .NAME C21 '%L'
    .LET C20=C12*C10               .NAME C1 '<Cu>'
    .LET C21=C12*C11               .NAME C2 'pH'
    .NAME C13 '(Cu)f'              .NAME C3 '<Cit>'
    .NAME C14 '%(Cu)'              .
```

```
*EXEC CDNO3
.LET K1=1/0.372
 RESULT=2.68817204
.LET K2=0.1*(10^0.31)
 RESULT=0.204173794
.LET K3=0.01/(0.78*0.78)
 RESULT=1.64365549E-2
.LET C3=10^(C2-9.99)
.LET C4=10^((C2*2)-20.3)
.LET C5=10^(C2-9.14)
.LET C6=10^((C2*2)-17.58)
.LET C7=1/(K1+K2+K3+C3+C4+C5+C6)
.LET C8=C1*C7
.LET C9=C7*K1
.NAME C9 '%Cd'
.LET C10=C7*C3
.NAME C10 '%HO1'
.LET C11=C7*C4
.NAME C11 '%HO2'
.LET C12=C7*C5
.NAME C12 '%HCO3'
.LET C13=C7*C6
.NAME C13 '%CO3'
.LET C14=C7*K2
.NAME C14 '%NO3'
.LET C15=C7*K3
.NAME C15 '%(NO3)2'
```

```
*EXEC CDSO4
.LET K1=1/0.372
 RESULT=2.68817204
.LET K2=3.49
 RESULT=3.49
.LET C3=10^(C2-9.99)
.LET C4=10^((2*C2)-20.30)
.LET C5=10^(C2-9.14)
.LET C6=10^((C2*2)-17.58)
.LET C7=1/(K1+K2+C3+C4+C5+C6)
.LET C8=C1*C7
.LET C9=C7*K1
.LET C10=C7*C3
.LET C11=C7*C4
.LET C12=C7*C5
.LET C13=C7*C6
.LET C14=C7*K2
    .NAME C1 'Cd tot' C2 'pH' C8 'Cd ACT' C9 '%Cd'
C10 '%HO1' C11 '%HO2' C12 '%HCO3' C13 '%CO3' C14 '%SO4'
```

```
ERASESAVE*EXEC CDCIT
.LET C4=C3/((10^(2.87-C2))+1.28*(10^(C2-3.92))+(10^((C2*2)-11.01)))
.LET C5=10^(C2-9.99)
.LET C6=10^((C2*2)-20.30)
.LET C7=10^(C2-9.14)
.LET C8=10^((C2*2)-17.58)
.LET C9=(10^1.08)*C4
.LET C10=(10^(C2-2.15))*C4
.LET C11=(10^((C2*2)-5.39))*C4
.LET K1=1/0.372
 RESULT=2.68817204
.LET C12
.LET C12=1/(K1+C11+C10+C9+C8+C7+C6+C5)
.LET C13=C12*C1
.LET C14=C12*K1
.LET C15=C12*C5
.LET C16=C12*C6
.LET C17=C12*C7
.LET C18=C12*C8
.LET C19=C12*C9
.LET C20=C12*C10
.LET C21=C12*C11
.NAME C1 '(Cd)'
.NAME C2 'pH'
.NAME C3 '(Cit)'
.NAME C13 '(Cd)'
.NAME C14 'Z(Cd)'
.NAME C15 'ZHO1'
.NAME C16 'ZHO2'
.NAME C17 'ZHCO3'
.NAME C18 'ZCO3'
.NAME C19 'ZH2L'
.NAME C20 'ZHL'
.NAME C21 'ZL'
```

```
 *EXEC CDCL
.LET K1=1/0.372
 RESULT=2.68817204
.LET K2=9.55
 RESULT=9.55
.LET K3=2.43
 RESULT=2.43
.LET K4=0.15
 RESULT=0.15
.LET K5=10^-4
 RESULT=1E-4
.LET C3=10^(C2-9.99)
.LET C4=10^((2*C2)-20.3)
.LET C5=10^(C2-9.14)
.LET C6=10^((2*C2)-17.58)
.LET C7=C3+C4+C5+C6+K1+K2+K3+K4+K5
.LET C8=1/C7
.LET C9=C1*C8
.LET C10=C8*K1
.LET C11=C8*C3
.LET C12=C8*C4
.LET C13=C8*C5
.LET C14=C8*C6
.LET C15=C8*K2
.LET C16=C8*K3
.LET C17=C8*K4
.LET C18=C8*K5
.NAME C1 TOTAL Cd
.NAME C2 pH
.NAME C9 Cd ACTIVTY
.NAME C10 HO1
.NAME C11 HO2
.NAME C12 HCO3
.NAME C13 HCO3
.NAME C14 CO3
.NAME C10 ZCd
.NAME C11 HO1
.NAME C12 HO2
.NAME C15 CdCl
.NAME C16 CdCl2
.NAME C17 CdCl3
.NAME C18 CdCl4
```

Appendix 2. Batch Isotherms by AAS, Batch Isotherms by AAS and ISE, Influence of Ashing and Influence of Initial pH; Cadmium and Copper.

batch isotherms: Copper. all concentrations are in uM, all sorbed figures are in uM/g of oven dry soil.

Arkleston			Arkleston High Zinc.			Caprington.			Dunlop.		
eq.	sorbed	susp. pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH
0.520	0.150	5.500	1.308	0.120	4.900	0.394	0.060	5.800	0.268	0.130	5.200
0.788	0.190	5.600	0.788	0.180	4.900	0.473	0.150	5.800	0.268	0.180	5.200
0.520	0.220	5.500	1.056	0.200	4.900	0.536	0.190	5.800	0.730	0.240	5.200
0.788	0.490	5.500	1.844	0.450	4.900	0.772	0.400	5.800	0.520	0.480	5.200
2.096	1.030	5.600	3.672	0.960	4.900	1.072	0.860	5.800	0.730	1.060	5.200
2.364	1.470	5.400	5.516	1.320	4.800			5.800	1.308	1.100	5.100
18.377	1.640	5.600	15.760	1.670	4.900			5.700	1.576	1.570	5.100
21.024	2.310	5.400	23.641	2.160	4.800			5.800			5.100
23.640	5.100	5.300	44.649	4.380	4.800	3.672	4.480	5.600	0.460	5.710	5.000
42.033	10.590	5.100	131.332	7.860	4.600	11.820	8.850	5.500	13.128	11.320	5.000
86.682	14.920	5.000	236.407	10.420	4.500	23.908	12.860	5.400	31.001	16.980	0.800
178.613	19.980	4.800	378.250	13.720	4.500	41.497	16.890	5.200	61.198	21.050	4.800

Blackstoun Alluvial.			Dreghorn.			Fen Arable.			Fen Subsoil.		
eq.	sorbed	susp.pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH
0.268	0.120	5.300	1.844	0.170	5.000	0.630	0.060	7.000	1.576	0.180	6.500
0.520	0.160	5.300	1.844	0.220	4.900	0.662	0.140	7.000	1.844	0.220	6.400
0.730	0.230	5.300	2.096	0.260	4.900	0.820	0.180	6.900	1.576	0.280	6.500
0.788	0.420	5.000	1.844	0.600	4.900	1.072	0.380	7.000	2.096	0.600	6.500
1.308	0.950	5.300	2.096	1.180	4.900			7.000	2.880	1.180	6.500
1.576	1.300	5.200	5.516	1.870	4.800			7.000	2.096	2.000	6.600
2.096	1.430	5.200	7.880	2.340	4.800	1.576	1.780	6.900	2.632	2.500	6.600
2.364	2.620	5.200	11.300	2.860	4.800	3.152	2.140	6.800	2.632	3.160	6.500
4.413	5.190	5.200	40.457	5.260	4.600	3.940	4.330	6.900	3.672	6.350	6.500
8.180	10.510	5.200	99.811	9.760	4.500	5.784	8.740	6.800	3.672	12.500	6.400
13.664	16.200	5.100	236.070	12.970	4.400	9.976	12.880	6.800	3.940	19.360	6.400
19.433	20.700	5.000	378.250	15.510	4.400	12.088	17.160	6.700	4.208	25.730	6.300

batch isotherms: Cadmium. all concentrations are in uM, all sorbed figures are in uM/g of oven dry soil.

Arkleston			Arkleston High Zinc.			Caprington.			Dunlop.		
eq.	sorbed	susp. pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH
0.650	0.170	5.600	2.140	0.120	4.900	0.240	0.170	5.700	0.600	0.180	5.300
0.830	0.210	5.500	2.730	0.150	4.900	0.470	0.200	5.700	0.650	0.220	5.300
1.800	0.460	5.500	5.690	0.340	4.900	1.070	0.450	5.700	1.840	0.480	5.300
4.210	0.850	5.500	12.220	0.590	4.900	2.610	0.840	5.700	4.210	0.900	5.300
7.000	1.310	5.600	22.540	0.850	4.900	4.150	1.350	5.700	6.160	1.450	5.300
10.200	1.650	5.500	32.030	1.010	4.900	5.990	1.680	5.700	9.610	1.790	5.300
14.230	1.960	5.400	2.700	1.140	4.900	7.830	2.000	5.700	16.370	1.970	5.300
45.080	3.620	5.500	99.640	2.020	4.800	22.530	3.920	5.600	36.770	3.960	5.200
130.490	6.230	5.300	222.420	3.540	4.800	74.110	7.210	5.500	106.760	7.110	5.100
222.420	8.110	5.200	344.010	0.580	4.800	112.700	10.650	5.400	183.870	9.800	5.100
349.640	9.980	5.200	510.080	5.360	4.700	65.240	16.690	5.500	106.760	17.420	5.100
652.430	5.860	5.200	462.630	10.660	4.700	320.280	14.340	5.400	349.930	15.110	5.100

Blackstoun Alluvial.			Dreghorn.			Fen Arable.			Fen Subsoil.		
eq.	sorbed	susp.pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH	eq.	sorbed	susp.pH
0.180	0.180	5.400	2.020	0.110	4.800	0.040	0.080	7.000	0.010	0.080	7.800
0.240	0.220	5.300	2.490	0.140	4.800	0.040	0.100	7.100	0.010	0.100	8.000
0.710	0.420	5.300	5.690	0.260	4.800	0.150	0.370	7.100	0.060	0.370	7.900
1.900	0.860	5.300	13.760	0.480	4.800	0.530	0.820	7.100	0.240	0.830	7.900
3.140	1.250	5.300	20.170	0.710	4.800	0.770	1.250	7.000	0.360	1.260	7.800
4.270	1.680	5.300	29.650	0.910	4.800	1.000	1.780	7.000	0.470	1.800	8.000
5.690	2.070	5.300	39.740	1.040	4.800	0.710	1.120	7.000	0.290	1.130	8.000
14.230	4.090	5.300	94.900	1.690	4.700	2.730	4.370	7.000	2.730	4.390	7.500
23.730	8.140	5.200	219.460	2.570	4.600	8.540	8.860	6.900	11.090	8.840	7.200
59.310	11.700	5.200	361.810	3.020	4.600	17.320	13.110	6.800	32.030	12.740	7.000
83.030	15.660	5.200	450.770	4.960	4.800	27.290	17.370	6.800	64.060	16.590	6.800
142.350	18.930	5.100	593.120	6.060	4.500	45.080	21.100	6.700	109.140	19.490	6.800

ise-batch data 7-8/88
soil: arkleston
element: cadmium ods cf: 0.907cd cf: 8.897fe cf: 17.905mn cf: 17.876 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	mn ppm	fe ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.000	1.814	0.000	0.002	0.140	0.340	0.000	0.021	1.540	61.510	0.002	-0.001	-0.001	2.503	6.088	5.50	4.25
2.030	1.841	0.070	0.005	0.090	0.350	0.623	0.046	2.870	113.510	0.004	0.029	0.016	1.609	6.267	5.45	4.20
1.990	1.805	0.160	0.013	0.100	0.510	1.423	0.112	3.370	130.930	0.009	0.066	0.036	1.788	9.132	5.48	4.65
2.050	1.859	0.240	0.020	0.120	0.550	2.135	0.178	3.850	216.850	0.021	0.098	0.053	2.145	9.848	5.44	4.42
2.020	1.832	0.620	0.050	0.090	0.460	5.516	0.445	2.730	313.450	0.034	0.254	0.138	1.609	8.236	5.56	4.28
1.990	1.805	1.390	0.130	0.100	0.360	12.367	1.157	11.570	639.810	0.090	0.560	0.311	1.788	6.446	5.30	4.20
1.990	1.805	1.800	0.180	0.110	0.350	16.014	1.601	11.970	645.200	0.120	0.721	0.399	1.966	6.267	5.42	4.38
2.000	1.814	2.600	0.360	0.130	0.360	23.132	3.203	23.030	2234.700	0.250	0.996	0.549	2.324	6.446	5.24	4.05
1.990	1.805	3.200	0.570	0.160	0.300	28.470	5.071	31.420	6017.800	0.390	1.170	0.648	2.860	5.372	5.20	4.15
2.000	1.814	6.900	0.660	0.150	0.320	61.388	5.872	33.050	1652.000	0.450	2.776	1.530	2.681	5.730	5.42	4.22
1.990	1.805	7.700	1.150	0.130	0.310	68.505	10.231	54.230	1652.000	0.790	2.914	1.614	2.324	5.551	5.35	4.26
2.010	1.823	10.400	1.150	0.090	0.300	92.527	10.231	48.220	1067.670	0.790	4.115	2.257	1.609	5.372	5.62	4.50

ise-batch data 7-8/88
soil: ahz
element: cadmium ods cf: 0.941cd cf: 8.897fe cf: 17.905mn cf: 18 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	mn ppm	fe ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.000	1.882	0.000	0.004	0.460	0.080	0.000	0.040	3	11	0.003	-0.002	-0.001	8.373	1.432	4.78	4.28
1.990	1.873	0.080	0.040	0.460	0.110	0.712	0.356	65	498	0.028	0.018	0.010	8.373	1.970	4.75	4.32
1.980	1.863	0.180	0.060	0.450	0.080	1.601	0.534	394	9966	0.041	0.053	0.029	8.191	1.432	4.72	4.26
1.990	1.873	0.260	0.090	0.410	0.050	2.313	0.801	28223	177400	0.062	0.076	0.040	7.463	0.895	4.76	4.30
1.980	1.863	0.640	0.240	0.420	0.090	5.694	2.135	1860	320800	0.160	0.178	0.096	7.645	1.611	4.76	4.22
1.990	1.873	1.360	0.540	0.440	0.090	12.100	4.804	38503	7311700	0.370	0.365	0.195	8.009	1.611	4.76	4.22
2.010	1.891	1.750	0.770	0.420	0.090	15.569	6.851	15680	2434600	0.530	0.436	0.230	7.645	1.611	4.75	4.30
1.990	1.873	2.700	1.210	0.400	0.090	24.021	10.765	252000	12831400	0.830	0.663	0.354	7.281	1.611	4.74	4.28
2.000	1.882	3.500	1.680	0.450	0.090	31.139	14.947	38500*********		1.160	0.810	0.430	8.191	1.611	4.72	4.20
2.010	1.891	5.200	2.500	0.480	0.090	46.263	22.242	35700*********		1.720	1.201	0.635	8.737	1.611	4.60	4.30
1.990	1.873	6.500	3.300	0.480	0.090	57.829	29.359	1697000*********		2.270	1.423	0.760	8.737	1.611	4.72	4.24
1.990	1.873	8.100	4.400	0.460	0.080	72.064	39.146	112000*********		3.030	1.646	0.879	8.373	1.432	4.70	4.04

ise-batch data 7-8/88
soil: caprington.
element: cadmium ods cf: 0.933cd cf: 8.897fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	mn ppm	fe ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.030	1.894	0.000	0.000	0.140	0.910	0.000	0.002	0.510	0.410	0.000	-0.000	-0.000	2.548	16.294	5.98	5.74
2.000	1.866	0.080	0.001	0.150	0.970	0.712	0.013	0.500	0.700	0.001	0.035	0.019	2.730	17.368	6.00	5.70
1.990	1.857	0.180	0.004	0.180	0.990	1.601	0.032	0.490	0.650	0.002	0.078	0.042	3.276	17.726	5.94	6.00
1.990	1.857	0.260	0.005	0.140	1.440	2.313	0.043	0.460	0.870	0.003	0.114	0.061	2.548	25.783	6.14	6.08
2.030	1.894	0.640	0.014	0.140	0.880	5.694	0.125	9.860	1.400	0.014	0.278	0.147	2.548	15.756	5.98	5.92
2.000	1.866	1.360	0.040	0.170	0.940	12.100	0.356	1.610	3.150	0.028	0.587	0.315	3.094	16.831	5.98	5.60
2.000	1.866	1.750	0.050	0.180	0.850	15.569	0.445	2.120	5.260	0.034	0.756	0.405	3.276	15.219	6.00	5.20
2.020	1.885	2.700	0.090	0.160	0.780	24.021	0.801	3.150	5.810	0.062	1.161	0.616	2.912	13.966	6.00	5.90
2.000	1.866	3.500	0.130	0.180	0.790	31.139	1.157	4.230	8.130	0.090	1.499	0.803	3.276	14.145	5.94	5.76
2.000	1.866	5.200	0.200	0.190	0.710	46.263	1.779	6.430	11.870	0.140	2.224	1.192	3.458	12.713	5.96	5.80
2.010	1.875	6.500	0.310	0.200	0.720	57.829	2.758	9.380	18.520	0.210	2.754	1.468	3.640	12.892	5.90	5.50
1.990	1.857	8.100	0.410	0.210	0.770	72.064	3.648	11.770	25.910	0.280	3.421	1.842	3.822	13.787	5.90	5.32

ise-batch data 7-8/88
soil: dunlop
element: cadmium ods cf: 0.834cd cf: 8.897fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	mn ppm	fe ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.010	1.676	0.000	0.000	0.150	0.210	0.000	0.000	0.970	1.290	0.000	0.000	0.000	2.730	3.760	5.14	4.46
1.990	1.660	0.080	0.005	0.130	0.210	0.712	0.044	1.250	1.690	0.003	0.033	0.020	2.366	3.760	5.10	4.48
1.990	1.660	0.180	0.012	0.090	0.200	1.601	0.103	1.740	3.310	0.008	0.075	0.045	1.638	3.581	5.10	4.36
1.980	1.651	0.260	0.018	0.120	0.220	2.313	0.160	1.660	3.700	0.012	0.108	0.065	2.184	3.939	5.10	4.45
1.980	1.651	0.640	0.060	0.130	0.220	5.694	0.534	3.540	6.380	0.041	0.258	0.156	2.366	3.939	5.10	4.40
2.000	1.668	1.360	0.130	0.120	0.180	12.100	1.157	6.650	13.240	0.090	0.547	0.328	2.184	3.223	5.12	4.46
2.010	1.676	1.750	0.190	0.130	0.230	15.569	1.690	8.630	18.520	0.130	0.694	0.414	2.366	4.118	5.12	4.40
2.010	1.676	2.700	0.320	0.150	0.180	24.021	2.847	13.690	30.130	0.220	1.059	0.632	2.730	3.223	5.12	4.40
2.000	1.668	3.500	0.450	0.120	0.180	31.139	4.004	18.670	38.120	0.310	1.357	0.813	2.184	3.223	5.12	4.40
1.990	1.660	5.200	0.760	0.150	0.150	46.263	6.762	29.140	55.610	0.520	1.975	1.190	2.730	2.686	5.10	4.42
1.990	1.660	6.500	1.100	0.130	0.200	57.829	9.786	40.090	86.770	0.760	2.402	1.447	2.366	3.581	5.06	4.38
2.010	1.676	8.100	1.390	0.140	0.180	72.064	12.367	49.030	107.940	0.960	2.985	1.781	2.548	3.223	5.08	4.32

ise-batch data 7-8/88
soil: blackstoun alluvial.
element: cadmium ods cf: 0.902cd cf: 8.897fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	mn ppm	fe ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
1.990	1.795	0.000	0.002	0.450	0.320	0.000	0.018	4.020	68.020	0.007	-0.001	-0.000	8.191	5.730	5.15	4.00
1.990	1.795	0.070	0.003	0.440	0.350	0.623	0.026	3.230	59.980	0.010	0.030	0.017	8.009	6.267	5.18	4.50
2.000	1.804	0.160	0.005	0.460	0.340	1.423	0.046	4.230	510.060	0.017	0.069	0.038	8.373	6.088	5.20	4.18
1.990	1.795	0.240	0.008	0.410	0.300	2.135	0.071	3.850	123.450	0.024	0.103	0.057	7.463	5.372	5.18	4.60
2.010	1.813	0.620	0.030	0.410	0.310	5.516	0.267	5.530	389.900	0.093	0.262	0.145	7.463	5.551	5.20	4.38
2.000	1.804	1.390	0.080	0.400	0.280	12.367	0.712	8.000	239.610	0.244	0.583	0.323	7.281	5.013	5.04	4.58
2.020	1.822	1.800	0.090	0.440	0.310	16.014	0.801	8.340	346.670	0.275	0.761	0.417	8.009	5.551	5.16	4.40
1.990	1.795	2.600	0.130	0.440	0.320	23.132	1.157	9.540	1023.780	0.399	1.099	0.612	8.009	5.730	5.30	4.30
2.000	1.804	3.200	0.220	0.460	0.320	28.470	1.957	13.800	1858.010	0.674	1.326	0.735	8.373	5.730	5.10	4.00
2.010	1.813	6.900	0.320	0.450	0.330	61.388	2.847	18.360	1781.640	0.980	2.927	1.614	8.191	5.909	5.12	4.30
2.000	1.804	7.700	0.560	0.500	0.330	68.505	4.982	28.650	1305.960	1.712	3.176	1.761	9.101	5.909	5.12	4.30
2.000	1.804	10.400	0.600	0.560	0.340	92.527	5.338	30.130	973.500	1.836	4.359	2.417	10.193	6.088	5.08	4.28

ise-batch data 7-8/88
soil: dreghorn
element: cadmium ods cf: 0.982cd cf: 8.897fe cf: 17.905mn cf: 18 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	mn ppm	fe ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
1.990	1.954	0.000	0.000	1.690	0.280	0.000	0.003	1	1	0.000	-0.000	-0.000	30.761	5.013	4.74	4.30
2.000	1.964	0.080	0.016	1.610	0.230	0.712	0.142	4	4	0.012	0.028	0.014	29.305	4.118	4.72	4.36
2.000	1.964	0.180	0.040	1.660	0.240	1.601	0.356	16	34	0.028	0.062	0.032	30.215	4.297	4.72	4.30
2.000	1.964	0.260	0.070	1.730	0.230	2.313	0.623	194	234	0.048	0.085	0.043	31.489	4.118	4.74	4.35
1.990	1.954	0.640	0.190	1.710	0.270	5.694	1.690	137	2022	0.130	0.200	0.102	31.125	4.834	4.74	4.22
1.980	1.944	1.360	0.450	1.710	0.230	12.100	4.004	640	19837	0.310	0.405	0.208	31.125	4.118	4.74	4.22
1.990	1.954	1.750	0.650	1.710	0.270	15.569	5.783	696	29483	0.450	0.489	0.250	31.125	4.834	4.70	4.22
2.000	1.964	2.700	1.080	1.740	0.300	24.021	9.609	2646	29190	0.740	0.721	0.367	31.671	5.372	4.74	4.28
1.990	1.954	3.500	1.530	1.850	0.300	31.139	13.612	1640	79250	1.050	0.876	0.448	33.673	5.372	4.72	4.24
2.000	1.964	5.200	2.400	1.820	0.250	46.263	21.352	1989	2394000	1.650	1.246	0.634	33.127	4.476	4.72	4.15
2.010	1.974	6.500	3.200	1.830	0.270	57.829	28.470	8787	1815000	2.200	1.468	0.744	33.309	4.834	4.70	4.18
1.990	1.954	8.100	4.100	1.950	0.190	72.064	36.477	5400	7625000	2.820	1.779	0.911	35.493	3.402	4.70	4.22

ise-batch data 7-8/88

soil: fen arable cd cf:

element: cadmium ods cf: 0.902 8.897 fe cf: 17.905an cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	fe ppm	ca ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	fe (uM)	ca (uM)	pH susp	pH super
2.020	1.822	0.000	0.000	0.220	79.000	0.000	0.002	0.510	0.240	0.000	-0.000	-0.000	3.939	1971.058	7.25	7.00
1.990	1.795	0.070	0.001	0.190	85.000	0.623	0.009	0.310	0.250	0.001	0.031	0.017	3.402	2120.758	7.35	7.45
2.000	1.804	0.160	0.003	0.230	87.000	1.423	0.027	0.260	0.250	0.002	0.070	0.039	4.118	2170.659	7.24	7.20
1.990	1.795	0.240	0.004	0.240	72.000	2.135	0.036	0.270	0.240	0.003	0.105	0.058	4.297	1796.407	7.28	7.24
1.990	1.795	0.620	0.006	0.230	83.000	5.516	0.053	0.280	0.300	0.004	0.273	0.152	4.118	2070.858	7.24	7.25
1.990	1.795	1.390	0.019	0.240	86.000	12.367	0.169	0.540	0.330	0.010	0.610	0.340	4.297	2145.709	7.40	7.36
2.010	1.813	1.800	0.028	0.240	90.000	16.014	0.249	0.550	0.420	0.015	0.788	0.435	4.297	2245.509	7.24	7.20
1.990	1.795	2.600	0.033	0.220	81.000	23.132	0.294	0.760	0.500	0.018	1.142	0.636	3.939	2020.958	7.30	7.28
2.000	1.804	3.200	0.044	0.600	88.000	28.470	0.391	0.900	0.570	0.024	1.404	0.778	10.743	2195.609	7.24	7.20
1.990	1.795	6.900	0.070	0.190	68.000	61.388	0.623	1.230	0.890	0.036	3.038	1.693	3.402	1696.607	7.24	7.28
1.990	1.795	7.700	0.100	0.210	74.000	68.505	0.890	1.970	1.490	0.069	3.381	1.883	3.760	1846.307	7.10	7.08
2.000	1.804	10.400	0.110	0.210	92.000	92.527	0.979	2.250	1.690	0.076	4.577	2.537	3.760	2295.409	7.02	7.16

ise-batch data 7-8/88

soil: fen subsoil cd cf:

element: cadmium ods cf: 0.960 8.897 fe cf: 17.905an cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init cd ppm	equil cd ppm	fe ppm	ca ppm	init cd (uM)	equil cd (uM)	ISE susp (uM)	ISE super (uM)	(Cd)f calc	cd upt. uM	cd upt. uM/ods	fe (uM)	ca (uM)	pH susp	pH super
1.990	1.910	0.000	0.000	0.031	85.000	0.000	0.001	0.320	0.250	0.000	-0.000	-0.000	0.555	2120.758	8.24	7.62
2.010	1.930	0.070	0.000	0.038	84.000	0.623	0.001	0.260	0.310	0.000	0.031	0.016	0.680	2095.808	8.24	7.64
1.980	1.901	0.160	0.000	0.033	81.000	1.423	0.004	0.250	0.330	0.000	0.071	0.037	0.591	2020.958	8.20	7.64
2.000	1.920	0.240	0.001	0.034	82.000	2.135	0.006	0.260	0.320	0.000	0.106	0.055	0.609	2045.908	8.26	7.64
2.000	1.920	0.620	0.002	0.027	93.000	5.516	0.022	0.220	0.320	0.002	0.275	0.143	0.483	2320.359	8.20	7.70
2.000	1.920	1.390	0.006	0.022	91.000	12.367	0.052	0.320	0.380	0.004	0.616	0.321	0.394	2270.459	8.20	7.62
2.000	1.920	1.800	0.009	0.028	47.000	16.014	0.076	0.430	0.430	0.006	0.797	0.415	0.501	1172.655	8.30	7.62
2.000	1.920	2.600	0.064	0.017	58.000	23.132	0.569	0.590	0.510	0.003	1.128	0.588	0.304	1447.106	8.28	7.52
2.010	1.930	3.200	0.088	0.016	97.000	28.470	0.783	0.670	0.590	0.005	1.384	0.717	0.286	2420.160	8.28	7.52
1.990	1.910	6.900	0.312	0.034	86.000	61.388	2.776	1.010	0.890	0.017	2.931	1.534	0.609	2145.709	8.20	7.54
2.010	1.930	7.700	0.324	0.036	97.000	68.505	2.883	1.560	1.290	0.018	3.281	1.700	0.645	2420.160	8.20	7.58
2.010	1.930	10.400	0.324	0.024	66.000	92.527	2.883	1.650	1.360	0.018	4.482	2.323	0.430	1646.707	8.04	7.60

ise-batch data 7-8/88
soil: arkleston
element: copper ods cf: 0.907cu cf: 15.736fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	mn ppm	fe ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.010	1.823	0.003	0.012	0.090	0.820	0.040	0.189	0.000	0.020	0.015	-0.007	-0.004	1.638	14.682	5.40	4.28
2.010	1.823	0.049	0.012	0.090	0.650	0.771	0.189	0.000	0.010	0.015	0.029	0.016	1.638	11.638	5.60	4.32
2.010	1.823	0.110	0.015	0.090	0.490	1.731	0.236	0.000	0.020	0.018	0.075	0.041	1.638	8.774	5.46	4.18
2.020	1.832	0.140	0.011	0.090	0.340	2.203	0.173	0.000	0.010	0.013	0.101	0.055	1.638	6.088	5.45	4.54
2.000	1.814	0.370	0.017	0.100	0.600	5.822	0.268	0.000	0.020	0.021	0.278	0.153	1.820	10.743	5.42	4.34
2.000	1.814	0.820	0.021	0.090	0.410	12.903	0.330	0.000	0.020	0.025	0.629	0.347	1.638	7.341	5.58	4.48
2.000	1.814	1.100	0.027	0.110	0.570	17.309	0.425	0.010	0.020	0.033	0.844	0.465	2.002	10.206	5.42	4.52
2.020	1.832	1.570	0.032	0.110	0.350	24.705	0.504	0.010	0.040	0.038	1.210	0.660	2.002	6.267	5.44	4.40
2.000	1.814	2.240	0.047	0.100	0.400	35.248	0.740	0.030	0.060	0.057	1.725	0.951	1.820	7.162	5.44	4.40
1.990	1.805	3.140	0.067	0.100	0.370	49.410	1.054	0.050	0.090	0.081	2.418	1.340	1.820	6.625	5.38	4.32
2.020	1.832	3.860	0.076	0.110	0.450	60.740	1.196	0.070	0.120	0.092	2.977	1.625	2.002	8.057	5.42	4.38
2.020	1.832	4.200	0.094	0.130	0.370	66.090	1.479	0.110	0.170	0.110	3.231	1.763	2.366	6.625	5.38	4.22

ise-batch data 7-8/88
soil: ahz
element: copper ods cf: 0.941cu cf: 15.736fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	mn ppm	fe ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
1.980	1.863	0.002	0.018	0.360	0.100	0.039	0.283	0.094	0.074	0.022	-0.012	-0.007	6.553	1.791	4.78	4.14
2.000	1.882	0.060	0.018	0.400	0.070	0.944	0.283	0.073	0.074	0.022	0.033	0.018	7.281	1.253	4.78	4.15
2.000	1.882	0.120	0.018	0.440	0.070	1.888	0.283	0.071	0.080	0.022	0.080	0.043	8.009	1.253	4.72	3.86
2.010	1.891	0.180	0.024	0.400	0.070	2.832	0.378	0.086	0.095	0.028	0.123	0.065	7.281	1.253	4.72	4.10
2.010	1.891	0.400	0.024	0.390	0.060	6.294	0.378	0.130	0.130	0.035	0.296	0.156	7.099	1.074	4.70	4.08
2.000	1.882	0.861	0.025	0.430	0.070	13.548	0.393	0.223	0.190	0.030	0.658	0.349	7.827	1.253	4.70	4.05
1.990	1.873	1.172	0.110	0.410	0.060	18.442	1.731	0.324	0.223	0.130	0.836	0.446	7.463	1.074	4.68	4.06
1.990	1.873	1.793	0.130	0.380	0.070	28.214	2.046	0.493	0.374	0.160	1.308	0.699	6.917	1.253	4.68	4.04
1.980	1.863	2.511	0.150	0.400	0.060	39.512	2.360	0.717	0.642	0.180	1.858	0.997	7.281	1.074	4.72	3.92
1.990	1.873	3.055	0.310	0.410	0.070	48.072	4.878	1.184	0.882	0.380	2.160	1.153	7.463	1.253	4.64	4.05
1.980	1.863	3.956	0.390	0.430	0.070	62.250	6.137	1.399	0.918	0.470	2.806	1.506	7.827	1.253	4.64	3.98
1.980	1.863	5.148	0.580	0.410	0.080	81.007	9.127	2.219	1.804	0.700	3.594	1.929	7.463	1.432	4.64	3.98

ise-batch data 7-8/88
soil: caprington.
element: copper ods cf: 0.933cu cf: 15.736fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	mn ppm	fe ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.020	1.885	0.002	0.019	0.220	0.850	0.039	0.299	0.001	0.001	0.023	-0.013	-0.007	4.004	15.219	6.06	5.74
2.000	1.866	0.060	0.019	0.200	0.760	0.944	0.299	0.000	0.001	0.023	0.032	0.017	3.640	13.608	6.00	5.10
2.000	1.866	0.120	0.025	0.200	0.780	1.888	0.393	0.000	0.000	0.030	0.075	0.040	3.640	13.966	6.02	5.80
1.990	1.857	0.180	0.025	0.190	0.790	2.832	0.393	0.000	0.000	0.030	0.122	0.066	3.458	14.145	6.00	5.90
2.000	1.866	0.400	0.031	0.190	0.750	6.294	0.488	0.000	0.002	0.038	0.290	0.156	3.458	13.429	5.98	4.72
1.980	1.847	0.861	0.041	0.210	0.700	13.548	0.645	0.000	0.001	0.049	0.645	0.349	3.822	12.534	5.98	5.30
2.000	1.866	1.172	0.045	0.220	0.860	18.442	0.708	0.001	0.001	0.054	0.887	0.475	4.004	15.398	5.96	5.62
2.020	1.885	1.793	0.064	0.220	0.770	28.214	1.007	0.001	0.002	0.078	1.360	0.722	4.004	13.787	5.94	5.58
2.010	1.875	2.511	0.071	0.210	0.640	39.512	1.117	0.001	0.002	0.086	1.920	1.024	3.822	11.459	5.90	5.62
1.990	1.857	3.055	0.081	0.230	0.560	48.072	1.275	0.006	0.009	0.098	2.340	1.260	4.186	10.027	5.92	5.18
1.980	1.847	3.956	0.094	0.220	0.800	62.250	1.479	0.005	0.007	0.110	3.039	1.645	4.004	14.324	5.88	5.48
2.000	1.866	5.148	0.112	0.230	0.700	81.007	1.762	0.003	0.007	0.140	3.962	2.123	4.186	12.534	5.90	5.46

ise-batch data 7-8/88
soil: dunlop
element: copper ods cf: 0.834cu cf: 15.736fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	mn ppm	fe ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.010	1.676	0.002	0.010	0.150	0.200	0.039	0.150	0.004	0.009	0.012	-0.006	-0.003	2.730	3.581	5.18	4.54
2.020	1.685	0.060	0.010	0.120	0.200	0.944	0.150	0.003	0.008	0.012	0.040	0.024	2.184	3.581	5.14	4.34
2.010	1.676	0.120	0.010	0.140	0.200	1.888	0.150	0.002	0.007	0.012	0.087	0.052	2.548	3.581	5.14	4.48
1.990	1.660	0.180	0.010	0.130	0.190	2.832	0.150	0.002	0.007	0.012	0.134	0.081	2.366	3.402	5.14	4.50
1.990	1.660	0.400	0.014	0.130	0.170	6.294	0.220	0.002	0.007	0.017	0.304	0.183	2.366	3.044	5.10	4.44
2.010	1.676	0.861	0.019	0.130	0.210	13.548	0.299	0.005	0.017	0.023	0.662	0.395	2.366	3.760	5.10	4.20
1.980	1.651	1.172	0.024	0.140	0.190	18.442	0.378	0.007	0.019	0.028	0.903	0.547	2.548	3.402	5.12	4.44
2.000	1.668	1.793	0.033	0.150	0.190	28.214	0.519	0.014	0.029	0.040	1.385	0.830	2.730	3.402	5.10	4.32
2.010	1.676	2.511	0.046	0.140	0.170	39.512	0.724	0.021	0.043	0.056	1.939	1.157	2.548	3.044	5.12	4.36
2.010	1.676	3.055	0.056	0.120	0.180	48.072	0.881	0.043	0.068	0.068	2.360	1.408	2.184	3.223	5.12	4.20
2.000	1.668	3.956	0.070	0.150	0.160	62.250	1.101	0.068	0.098	0.085	3.057	1.833	2.730	2.865	5.08	4.36
2.000	1.668	5.148	0.088	0.110	0.200	81.007	1.385	0.091	0.129	0.110	3.981	2.387	2.002	3.581	5.12	4.34

ise-batch data 7-8/88
soil: blackstoun alluvial.
element: copper ods cf: 0.902cu cf: 15.736fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	mn ppm	fe ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.010	1.813	0.003	0.021	0.500	0.300	0.040	0.330	0.010	0.010	0.025	-0.015	-0.008	9.101	5.372	5.32	4.52
2.000	1.804	0.049	0.021	0.530	0.290	0.771	0.330	0.000	0.010	0.025	0.022	0.012	9.647	5.192	5.20	4.48
2.020	1.822	0.110	0.020	0.480	0.270	1.731	0.315	0.000	0.000	0.024	0.071	0.039	8.737	4.834	5.30	4.62
2.000	1.804	0.140	0.021	0.520	0.270	2.203	0.330	0.000	0.000	0.025	0.094	0.052	9.465	4.834	5.24	4.54
1.980	1.786	0.370	0.026	0.550	0.270	5.822	0.409	0.000	0.000	0.031	0.271	0.152	10.011	4.834	5.20	4.65
1.990	1.795	0.820	0.034	0.520	0.290	12.903	0.535	0.000	0.010	0.042	0.618	0.345	9.465	5.192	5.24	4.40
2.000	1.804	1.100	0.034	0.550	0.310	17.309	0.535	0.000	0.020	0.042	0.839	0.465	10.011	5.551	5.20	4.20
2.020	1.822	1.570	0.047	0.490	0.250	24.705	0.740	0.010	0.020	0.057	1.198	0.658	8.919	4.476	5.20	4.44
1.980	1.786	2.240	0.054	0.530	0.240	35.248	0.850	0.010	0.020	0.065	1.720	0.963	9.647	4.297	5.20	4.60
2.000	1.804	3.140	0.072	0.500	0.250	49.410	1.133	0.010	0.020	0.087	2.414	1.338	9.101	4.476	5.18	4.50
1.990	1.795	3.860	0.085	0.520	0.250	60.740	1.338	0.020	0.030	0.100	2.970	1.655	9.465	4.476	5.20	4.60
2.000	1.804	4.200	0.092	0.560	0.340	66.090	1.448	0.030	0.050	0.110	3.232	1.792	10.193	6.088	5.26	4.64

ise-batch data 7-8/88
soil: dreghorn
element: copper ods cf: 0.982cu cf: 15.736fe cf: 17.905mn cf: 18.202 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	mn ppm	fe ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	mn (uM)	fe (uM)	pH susp	pH super
2.010	1.974	0.002	0.008	1.700	0.300	0.039	0.123	0.076	0.019	0.009	-0.004	-0.002	30.943	5.372	4.74	4.32
2.010	1.974	0.060	0.009	1.560	0.290	0.944	0.134	0.020	0.017	0.010	0.041	0.021	28.395	5.192	4.68	4.12
1.990	1.954	0.120	0.009	1.630	0.250	1.888	0.134	0.012	0.017	0.010	0.088	0.045	29.669	4.476	4.66	4.20
2.000	1.964	0.180	0.012	1.620	0.240	2.832	0.189	0.010	0.020	0.015	0.132	0.067	29.487	4.297	4.68	4.00
2.010	1.974	0.400	0.014	1.600	0.240	6.294	0.220	0.018	0.030	0.017	0.304	0.154	29.123	4.297	4.66	4.12
2.020	1.984	0.861	0.026	1.660	0.270	13.548	0.409	0.044	0.056	0.032	0.657	0.331	30.215	4.834	4.70	4.12
1.970	1.935	1.172	0.033	1.690	0.240	18.442	0.519	0.073	0.079	0.040	0.896	0.463	30.761	4.297	4.62	4.10
1.990	1.954	1.793	0.053	1.790	0.230	28.214	0.834	0.158	0.142	0.065	1.369	0.701	32.581	4.118	4.64	4.05
2.000	1.964	2.511	0.140	1.680	0.190	39.512	2.203	0.297	0.285	0.170	1.865	0.950	30.579	3.402	4.62	4.05
1.990	1.954	3.055	0.220	1.700	0.250	48.072	3.462	0.539	0.386	0.270	2.231	1.141	30.943	4.476	4.56	4.12
1.980	1.944	3.956	0.330	1.710	0.260	62.250	5.193	0.875	0.662	0.400	2.853	1.467	31.125	4.655	4.60	4.05
2.030	1.993	5.148	0.400	1.840	0.220	81.007	6.294	1.156	0.821	0.480	3.736	1.874	33.491	3.939	4.58	4.10

ise-batch data 7-8/88
soil: fen arable. cu cf:
element: copper ods cf: 0.958 15.736 fe cf: 17.905 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	fe ppm	ca ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	fe (uM)	ca (uM)	pH susp	pH super
1.990	1.906	0.003	0.022	0.240	60.000	0.040	0.346	0.000035	0.000021	0.020	-0.015	-0.008	4.297	1497.006	7.30	7.14
1.980	1.897	0.049	0.022	0.160	70.000	0.771	0.346	0.000026	0.000014	0.014	0.021	0.011	2.865	1746.507	7.24	7.40
2.000	1.916	0.110	0.029	0.150	75.000	1.731	0.456	0.000022	0.000013	0.022	0.064	0.033	2.686	1871.257	7.24	7.30
1.980	1.897	0.140	0.032	0.270	67.000	2.203	0.504	0.000019	0.000023	0.030	0.085	0.045	4.834	1671.657	7.24	7.14
1.990	1.906	0.370	0.034	0.210	67.000	5.822	0.535	0.000018	0.000014	0.024	0.264	0.139	3.760	1671.657	7.24	7.34
1.990	1.906	0.820	0.049	0.170	74.000	12.903	0.771	0.000018	0.000013	0.037	0.607	0.318	3.044	1846.307	7.28	7.34
2.020	1.935	1.100	0.068	0.180	73.000	17.309	1.070	0.000021	0.000015	0.039	0.812	0.420	3.223	1821.357	7.20	7.30
2.020	1.935	1.570	0.085	0.170	73.000	24.705	1.338	0.000025	0.000019	0.061	1.168	0.604	3.044	1821.357	7.24	7.44
2.010	1.926	2.240	0.110	0.170	58.000	35.248	1.731	0.000034	0.000027	0.087	1.676	0.870	3.044	1447.106	7.20	7.34
2.000	1.916	3.140	0.123	0.170	78.000	49.410	1.935	0.000048	0.000042	0.094	2.374	1.239	3.044	1946.108	7.18	7.28
1.990	1.906	3.860	0.129	0.170	61.000	60.740	2.030	0.000066	0.000053	0.095	2.935	1.540	3.044	1521.956	7.20	7.30
2.010	1.926	4.200	0.164	0.140	63.000	66.090	2.581	0.000090	0.000073	0.120	3.175	1.649	2.507	1571.856	7.22	7.32

ise-batch data 7-8/88
soil: fen subsoil. cu cf:
element: copper ods cf: 0.960 15.736 fe cf: 17.905 ca cf 24.950

air dry (g)	oven dry (g)	init.cu ppm	equil.cu ppm	fe ppm	ca ppm	init cu (uM)	equil cu (uM)	ISE susp (uM)	ISE super (uM)	(cu)f calc	cu upt. uM	cu upt. uM/ods	fe (uM)	ca (uM)	pH susp	pH super
2.000	1.920	0.003	0.012	0.160	81.000	0.040	0.189	0.000009	0.000013	0.003	-0.007	-0.004	2.865	2020.958	8.18	7.70
1.990	1.910	0.049	0.013	0.100	79.000	0.771	0.205	0.000008	0.000011	0.004	0.028	0.015	1.791	1971.058	8.18	7.70
1.990	1.910	0.110	0.029	0.040	74.000	1.731	0.456	0.000006	0.000014	0.011	0.064	0.033	0.716	1846.307	8.20	7.60
2.010	1.930	0.140	0.016	0.040	64.000	2.203	0.252	0.000005	0.000012	0.005	0.098	0.051	0.716	1596.806	8.20	7.65
1.980	1.901	0.370	0.015	0.040	73.000	5.822	0.236	0.000005	0.000010	0.004	0.279	0.147	0.716	1821.357	8.24	7.68
2.010	1.930	0.820	0.028	0.060	75.000	12.903	0.441	0.000005	0.000012	0.008	0.623	0.323	1.074	1871.257	8.15	7.68
1.990	1.910	1.100	0.029	0.050	87.000	17.309	0.456	0.000006	0.000014	0.008	0.843	0.441	0.895	2170.659	8.24	7.70
1.990	1.910	1.570	0.039	0.050	92.000	24.705	0.614	0.000007	0.000021	0.011	1.205	0.631	0.895	2295.409	8.24	7.68
2.010	1.930	2.240	0.055	0.040	90.000	35.248	0.865	0.000008	0.000044	0.023	1.719	0.891	0.716	2245.509	8.30	7.56
1.980	1.901	3.140	0.062	0.040	85.000	49.410	0.976	0.000011	0.000043	0.018	2.422	1.274	0.716	2120.758	8.28	7.68
1.990	1.910	3.860	0.070	0.230	83.000	60.740	1.101	0.000015	0.000063	0.022	2.982	1.561	4.118	2070.858	8.25	7.65
1.990	1.910	4.200	0.070	0.053	98.000	66.090	1.101	0.000021	0.000090	0.023	3.249	1.701	0.949	2445.110	8.26	7.64

ashed soil adsorption.
soil: arkleston
element: Copper Cu cf: 15.736

soil wt.	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uMoles	soil upt. uMol/g
2.010	5.640	0.270	0.006	4.249	0.094	0.208	0.103
2.000	5.240	0.600	0.009	9.441	0.135	0.465	0.233
2.010	5.580	0.920	0.008	14.477	0.123	0.718	0.357
2.000	5.440	1.260	0.014	19.827	0.225	0.980	0.490
2.010	5.420	1.570	0.017	24.705	0.261	1.222	0.608
2.000	5.660	1.910	0.021	30.055	0.324	1.487	0.743

ashed soil adsorption.
soil: ahz
element: Copper Cu cf: 15.736

soil wt.	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uMoles	soil upt. uMol/g
2.010	5.180	0.270	0.010	4.249	0.154	0.205	0.102
2.000	5.180	0.600	0.020	9.441	0.318	0.456	0.228
2.020	5.180	0.920	0.016	14.477	0.255	0.711	0.352
2.000	5.380	1.260	0.021	19.827	0.326	0.975	0.488
2.010	5.300	1.570	0.020	24.705	0.318	1.219	0.607
2.000	5.240	1.910	0.034	30.055	0.535	1.476	0.738

ashed soil adsorption.
soil: fen arable
element: Copper Cu cf: 15.736

soil wt.	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uMoles	soil upt. uMol/g
2.000	7.680	0.270	0.002	4.249	0.035	0.211	0.105
2.000	7.780	0.600	0.003	9.441	0.050	0.470	0.235
2.000	7.860	0.920	0.002	14.477	0.028	0.722	0.361
2.000	7.720	1.260	0.002	19.827	0.030	0.990	0.495
2.000	7.700	1.570	0.002	24.705	0.030	1.234	0.617
2.000	7.920	1.910	0.003	30.055	0.047	1.500	0.750

ashed soil adsorption.
soil: arkleston
element: Cadmium Cd cf: 8.897

soil wt.	super pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM	final Cd uM	uptake uMoles	soil upt. uMol/g
2.000	6.480	0.540	0.060	4.804	0.534	0.214	0.107
2.010	6.480	1.040	0.160	9.253	1.423	0.391	0.195
2.010	6.460	1.730	0.270	15.391	2.402	0.649	0.323
2.010	5.740	2.320	0.420	20.641	3.737	0.845	0.420
2.010	5.740	2.810	0.500	25.000	4.448	1.028	0.511
2.010	5.620	3.320	0.690	29.537	6.139	1.170	0.582

ashed soil adsorption.
soil: ahz
element: Cadmium Cd cf: 8.897

soil wt.	super pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM	final Cd uM	uptake uMoles	soil upt. uMol/g
2.020	5.680	0.540	0.090	4.804	0.801	0.200	0.099
2.000	5.740	1.040	0.200	9.253	1.779	0.374	0.187
2.000	5.620	1.730	0.350	15.391	3.114	0.614	0.307
2.000	5.720	2.320	0.460	20.641	4.093	0.827	0.414
2.000	5.640	2.810	0.680	25.000	6.050	0.948	0.474
2.020	5.800	3.320	0.850	29.537	7.562	1.099	0.544

ashed soil adsorption.
soil: fen arable
element: Cdamium Cd cf: 8.897

soil wt.	super pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM	final Cd uM	uptake uMoles	soil upt. uMol/g
2.020	7.100	0.540	0.003	4.804	0.024	0.239	0.118
2.000	7.320	1.040	0.002	9.253	0.020	0.462	0.231
2.000	7.320	1.730	0.004	15.391	0.037	0.768	0.384
2.000	7.280	2.320	0.006	20.641	0.051	1.029	0.515
2.000	7.320	2.810	0.007	25.000	0.067	1.247	0.623
2.000	7.320	3.320	0.010	29.537	0.085	1.473	0.736

pH influence on uptake.
soil: arkleston soil cf: 0.907
element: Copper Cu cf: 15.736

soil wt. air	soil wt. oven	init.pH	eq. super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uMoles	uptake uMoles/g
2.000	1.814	4.000	4.840	1.000	0.028	15.736	0.439	0.765	0.422
2.010	1.823	5.000	4.880	0.360	0.016	5.665	0.253	0.271	0.148
2.000	1.814	6.000	4.920	0.940	0.027	14.792	0.431	0.718	0.396
2.000	1.814	7.000	4.780	0.900	0.030	14.162	0.466	0.685	0.378
2.010	1.823	8.000	4.900	0.830	0.026	13.061	0.411	0.632	0.347

pH influence on uptake.
soil: ahz soil cf: 0.941
element: Copper Cu cf: 15.736

soil wt. air	soil wt. oven	init.pH	eq. super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uMoles	uptake uMoles/g
2.000	1.882	4.000	4.440	1.000	0.084	15.736	1.327	0.720	0.383
2.000	1.882	5.000	4.540	0.360	0.047	5.665	0.738	0.246	0.131
2.000	1.882	6.000	4.540	0.940	0.076	14.792	1.190	0.680	0.361
2.000	1.882	7.000	4.540	0.900	0.067	14.162	1.061	0.655	0.348
2.010	1.891	8.000	4.580	0.830	0.065	13.061	1.021	0.602	0.318

pH influence on uptake.
soil: f.arable soil cf: 0.958
element: Copper Cu cf: 15.736

soil wt. air	soil wt. oven	init.pH	eq. super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uMoles	uptake uMoles/g
2.010	1.926	4.000	7.120	1.000	0.058	15.736	0.916	0.741	0.385
2.000	1.916	5.000	7.220	0.360	0.040	5.665	0.631	0.252	0.131
2.000	1.916	6.000	7.220	0.940	0.059	14.792	0.928	0.693	0.362
2.010	1.926	7.000	7.360	0.900	0.058	14.162	0.921	0.662	0.344
2.010	1.926	8.000	7.280	0.830	0.058	13.061	0.919	0.607	0.315

pH influence on uptake.
soil: arkleston. soil cf: 0.907
element: Cadmium Cd cf: 8.897

soil wt. air	soil wt. oven	init.pH	eq. super pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM	final Cd uM	uptake uMoles	uptake uMoles/g
1.990	1.805	4.000	4.780	1.550	0.199	13.790	1.770	0.601	0.333
2.000	1.814	5.000	4.780	1.550	0.186	13.790	1.655	0.607	0.334
2.000	1.814	6.000	4.820	1.550	0.182	13.790	1.619	0.609	0.335
2.000	1.814	7.000	4.820	1.550	0.177	13.790	1.575	0.611	0.337
2.000	1.814	8.000	4.820	1.550	0.173	13.790	1.539	0.613	0.338

pH influence on uptake.
soil: ahz soil cf: 0.941
element: Cadmium Cd cf: 8.897

soil wt. air	soil wt. oven	init.pH	eq. super pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM	final Cd uM	uptake uMoles	uptake uMoles/g
2.000	1.882	4.000	4.380	1.550	0.750	13.790	6.673	0.356	0.189
2.000	1.882	5.000	4.440	1.550	0.710	13.790	6.317	0.374	0.199
2.000	1.882	6.000	4.420	1.550	0.720	13.790	6.406	0.369	0.196
1.990	1.873	7.000	4.480	1.550	0.710	13.790	6.317	0.374	0.200
2.000	1.882	8.000	4.460	1.550	0.680	13.790	6.050	0.387	0.206

pH influence on uptake.
soil: f.arable soil cf: 0.958
element: Cadmium Cd cf: 8.897

soil wt. air	soil wt. oven	init.pH	eq. super pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM	final Cd uM	uptake uMoles	uptake uMoles/g
1.990	1.906	4.000	7.100	1.550	0.016	13.790	0.139	0.683	0.358
1.990	1.906	5.000	7.160	1.550	0.016	13.790	0.140	0.683	0.358
2.000	1.916	6.000	7.220	1.550	0.015	13.790	0.137	0.683	0.356
2.010	1.926	7.000	7.220	1.550	0.015	13.790	0.129	0.683	0.355
2.010	1.926	8.000	7.180	1.550	0.014	13.790	0.127	0.683	0.355

Appendix 3: Cation Competition Data Tables: Influence upon Cadmium and Copper.

coapetitive uptake: Cd vs K
soil: arkleston
oven dry cf: 0.907 Cd cf: 8.897 K cf: 25.575

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. K ug/ml	final Cd ug/ml	final K ug/ml	init. Cd uM/l	init. K uM/l	final Cd uM/l	final K uM/l	Cadmium uptake uM	Cadmium soil up take uM/g	Potassium uptake uM	Potassium soil up take uM/
1.990	1.805	4.260	0.480	0.050	0.040	4.250	4.270	1.279	0.356	108.696	0.196	0.108	-5.371	-2.97
2.010	1.823	4.420	0.980	0.050	0.100	4.350	8.719	1.279	0.890	111.253	0.391	0.215	-5.499	-3.01
1.990	1.805	4.240	1.540	0.050	0.160	4.350	13.701	1.279	1.423	111.253	0.614	0.340	-5.499	-3.04
1.990	1.805	4.320	2.400	0.050	0.210	4.250	21.352	1.279	1.868	108.696	0.974	0.540	-5.371	-2.97
1.990	1.805	4.440	3.000	0.050	0.280	4.050	26.690	1.279	2.491	103.581	1.210	0.670	-5.115	-2.83
1.990	1.805	4.080	3.200	0.050	0.380	4.250	28.470	1.279	3.381	108.696	1.254	0.695	-5.371	-2.97
1.990	1.805	4.380	0.500	0.450	0.050	4.900	4.448	11.509	0.445	125.320	0.200	0.111	-5.691	-3.15
2.010	1.823	4.420	0.990	0.450	0.100	4.900	8.808	11.509	0.890	125.320	0.396	0.217	-5.691	-3.12
1.990	1.805	4.460	1.520	0.450	0.150	4.900	13.523	11.509	1.335	125.320	0.609	0.338	-5.691	-3.15
2.000	1.814	4.420	2.400	0.450	0.210	4.900	21.352	11.509	1.868	125.320	0.974	0.537	-5.691	-3.13
2.010	1.823	4.460	2.900	0.450	0.270	4.700	25.801	11.509	2.402	120.205	1.170	0.642	-5.435	-2.98
2.000	1.814	4.520	3.300	0.450	0.340	4.700	29.359	11.509	3.025	120.205	1.317	0.726	-5.435	-2.99
2.010	1.823	4.480	0.480	2.200	0.040	6.100	4.270	56.266	0.356	156.010	0.196	0.107	-4.987	-2.73
1.990	1.805	4.440	0.980	2.200	0.090	6.000	8.719	56.266	0.801	153.453	0.396	0.219	-4.859	-2.69
2.000	1.814	4.480	1.520	2.200	0.150	6.000	13.523	56.266	1.335	153.453	0.609	0.336	-4.859	-2.67
2.000	1.814	5.320	2.400	2.200	0.150	6.100	21.352	56.266	1.335	156.010	1.001	0.552	-4.987	-2.74
2.000	1.814	4.560	2.700	2.200	0.270	5.900	24.021	56.266	2.402	150.895	1.081	0.596	-4.731	-2.60
2.000	1.814	4.500	3.250	2.200	0.340	6.100	28.915	56.266	3.025	156.010	1.294	0.714	-4.987	-2.74

coapetitive uptake: Cd vs K
soil: ahz
oven dry cf: 0.941 Cd cf: 8.897 K cf: 25.575

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. K ug/ml	final Cd ug/ml	final K ug/ml	init. Cd uM/l	init. K uM/l	final Cd uM/l	final K uM/l	Cadmium uptake uM	Cadmium soil up take uM/g	Potassium uptake uM	Potassium soil up take uM/g
1.990	1.873	4.160	0.480	0.050	0.190	4.600	4.270	1.279	1.690	117.647	0.129	0.069	-5.818	-3.107
2.000	1.882	4.160	0.980	0.050	0.380	4.900	8.719	1.279	3.381	125.320	0.267	0.142	-6.202	-3.295
1.980	1.863	3.860	1.540	0.050	0.600	4.600	13.701	1.279	5.338	117.647	0.418	0.224	-5.818	-3.123
2.010	1.891	3.920	2.400	0.050	0.830	4.600	21.352	1.279	7.384	117.647	0.698	0.369	-5.818	-3.076
2.000	1.882	4.160	3.000	0.050	1.070	4.600	26.690	1.279	9.520	117.647	0.859	0.456	-5.818	-3.092
2.010	1.891	4.100	3.200	0.050	1.270	4.900	28.470	1.279	11.299	125.320	0.859	0.454	-6.202	-3.279
2.000	1.882	4.140	0.500	0.450	0.200	5.050	4.448	11.509	1.779	129.156	0.133	0.071	-5.882	-3.126
2.000	1.882	4.140	0.990	0.450	0.400	5.050	8.808	11.509	3.559	129.156	0.262	0.139	-5.882	-3.126
2.000	1.882	4.180	1.520	0.450	0.600	5.050	13.523	11.509	5.338	129.156	0.409	0.217	-5.882	-3.126
2.000	1.882	4.200	2.400	0.450	0.790	5.050	21.352	11.509	7.028	129.156	0.716	0.381	-5.882	-3.126
2.020	1.901	4.180	2.900	0.450	1.020	5.250	25.801	11.509	9.075	134.271	0.836	0.440	-6.138	-3.229
2.000	1.882	4.080	3.300	0.450	1.270	5.250	29.359	11.509	11.299	134.271	0.903	0.480	-6.138	-3.261
1.990	1.873	4.200	0.480	2.200	0.170	6.700	4.270	56.266	1.512	171.355	0.138	0.074	-5.754	-3.073
1.990	1.873	4.240	0.980	2.200	0.390	6.800	8.719	56.266	3.470	173.913	0.262	0.140	-5.882	-3.141
1.990	1.873	4.160	1.520	2.200	0.620	6.700	13.523	56.266	5.516	171.355	0.400	0.214	-5.754	-3.073
2.000	1.882	4.140	2.400	2.200	0.880	7.000	21.352	56.266	7.829	179.028	0.676	0.359	-6.138	-3.261
1.980	1.863	4.180	2.700	2.200	1.100	7.400	24.021	56.266	9.786	189.258	0.712	0.382	-6.650	-3.569
2.020	1.901	4.160	3.250	2.200	1.380	6.600	28.915	56.266	12.278	168.798	0.832	0.438	-5.627	-2.960

coapetitive uptake: Cd vs K
soil: fen arable
oven dry cf: 0.958 Cd cf: 8.897 K cf: 25.575

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. K ug/ml	final Cd ug/ml	final K ug/ml	init. Cd uM/l	init. K uM/l	final Cd uM/l	final K uM/l	Cadmium uptake uM	Cadmium soil up take uM/g	Potassium uptake uM	Potassium soil up take uM/g
2.000	1.916	7.180	0.480	0.050	0.008	25.000	4.270	1.279	0.071	588.235	0.210	0.110	-29.348	-15.317
1.980	1.897	7.040	0.980	0.050	0.016	10.000	8.719	1.279	0.142	255.754	0.429	0.226	-12.724	-6.708
2.000	1.916	7.140	1.540	0.050	0.024	10.000	13.701	1.279	0.214	255.754	0.674	0.352	-12.724	-6.641
1.980	1.897	7.180	2.400	0.050	0.029	9.000	21.352	1.279	0.258	230.179	1.055	0.556	-11.445	-6.034
1.990	1.906	7.100	3.000	0.050	0.042	9.000	26.690	1.279	0.374	230.179	1.316	0.690	-11.445	-6.003
2.020	1.935	6.800	3.200	0.050	0.066	9.000	28.470	1.279	0.587	230.179	1.394	0.720	-11.445	-5.914
1.990	1.906	7.140	0.500	0.450	0.017	28.000	4.448	11.509	0.151	716.113	0.215	0.113	-35.230	-18.480
2.000	1.916	7.280	0.990	0.450	0.022	17.500	8.808	11.509	0.196	447.570	0.431	0.225	-21.803	-11.379
1.990	1.906	7.240	1.520	0.450	0.028	10.000	13.523	11.509	0.249	255.754	0.664	0.348	-12.212	-6.406
2.000	1.916	7.200	2.400	0.450	0.033	11.000	21.352	11.509	0.294	281.330	1.053	0.550	-13.491	-7.041
1.990	1.906	7.300	2.900	0.450	0.037	10.000	25.801	11.509	0.329	255.754	1.274	0.668	-12.212	-6.406
2.010	1.926	7.220	3.300	0.450	0.050	10.000	29.359	11.509	0.445	255.754	1.446	0.751	-12.212	-6.342
2.000	1.916	6.840	0.480	2.200	0.018	25.000	4.270	56.266	0.160	639.386	0.206	0.107	-29.156	-15.217
1.990	1.906	6.500	0.980	2.200	0.018	12.000	8.719	56.266	0.160	306.905	0.428	0.224	-12.532	-6.574
2.020	1.935	7.020	1.520	2.200	0.022	12.000	13.523	56.266	0.196	306.905	0.666	0.344	-12.532	-6.476
1.990	1.906	7.040	2.400	2.200	0.027	11.000	21.352	56.266	0.240	281.330	1.056	0.554	-11.253	-5.903
2.000	1.916	7.050	2.700	2.200	0.033	11.000	24.021	56.266	0.294	281.330	1.186	0.619	-11.253	-5.873
2.000	1.916	6.900	3.250	2.200	0.047	11.000	28.915	56.266	0.418	281.330	1.425	0.744	-11.253	-5.873

coapetitive uptake: Cd vs Cu
soil: arkleston
oven dry cf: 0.907 Cd cf: 8.897 Cu cf: 15.738

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Cu ug/ml	final Cd ug/ml	final Cu ug/ml	init. Cd uM/l	init. Cu uM/l	final Cd uM/l	final Cu uM/l	Cadmium uptake uM	Cadmium soil up_take uM/g	Copper uptake uM	Copper soil up_take uM/g
2.000	1.814	4.460	0.544	0.241	0.047	0.021	4.840	3.793	0.418	0.331	0.221	0.122	0.173	0.095
1.990	1.805	4.360	1.041	0.241	0.106	0.023	9.262	3.793	0.943	0.362	0.416	0.230	0.172	0.095
1.990	1.805	4.460	1.527	0.241	0.178	0.021	13.585	3.793	1.584	0.331	0.600	0.332	0.173	0.096
2.000	1.814	4.440	2.367	0.241	0.237	0.021	21.059	3.793	2.109	0.331	0.948	0.522	0.173	0.095
1.990	1.805	4.480	3.195	0.241	0.308	0.018	28.425	3.793	2.740	0.283	1.284	0.712	0.175	0.097
1.990	1.805	4.480	3.432	0.241	0.367	0.020	30.534	3.793	3.265	0.315	1.363	0.755	0.174	0.096
2.010	1.823	4.540	0.556	0.904	0.039	0.034	4.947	14.227	0.347	0.535	0.230	0.126	0.685	0.376
2.010	1.823	4.500	1.077	0.904	0.091	0.036	9.582	14.227	0.810	0.567	0.439	0.241	0.683	0.375
1.990	1.805	4.500	1.574	0.904	0.156	0.036	14.004	14.227	1.388	0.567	0.631	0.349	0.683	0.378
2.020	1.832	4.520	2.604	0.904	0.208	0.034	23.167	14.227	1.851	0.535	1.066	0.582	0.685	0.374
2.000	1.814	4.540	2.840	0.904	0.312	0.034	25.267	14.227	2.776	0.535	1.125	0.620	0.685	0.377
1.990	1.805	4.460	3.432	0.904	0.402	0.036	30.534	14.227	3.577	0.567	1.348	0.747	0.683	0.378
2.000	1.814	4.540	0.545	3.892	0.051	0.055	4.849	61.253	0.454	0.866	0.220	0.121	3.019	1.664
2.000	1.814	4.520	1.065	3.892	0.130	0.055	9.475	61.253	1.157	0.866	0.416	0.229	3.019	1.664
1.990	1.805	4.480	1.584	3.892	0.210	0.074	14.093	61.253	1.868	1.165	0.611	0.339	3.004	1.665
2.020	1.832	4.640	2.597	3.892	0.268	0.074	23.105	61.253	2.384	1.165	1.036	0.565	3.004	1.640
2.000	1.814	4.560	2.727	3.892	0.370	0.075	24.262	61.253	3.292	1.180	1.048	0.578	3.004	1.656
2.020	1.832	4.700	3.117	3.892	0.398	0.055	27.731	61.253	3.541	0.866	1.210	0.660	3.019	1.648

coapetitive uptake: Cd vs Cu
soil: ahz
oven dry cf: 0.941 Cd cf: 8.897 Cu cf: 15.738

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Cu ug/ml	final Cd ug/ml	final Cu ug/ml	init. Cd uM/l	init. Cu uM/l	final Cd uM/l	final Cu uM/l	Cadmium uptake uM	Cadmium soil up_take uM/g	Copper uptake uM	Copper soil up_take uM/g
2.000	1.882	4.140	0.544	0.241	0.213	0.055	4.840	3.793	1.895	0.866	0.147	0.078	0.146	0.078
2.020	1.901	4.160	1.041	0.241	0.426	0.055	9.262	3.793	3.790	0.866	0.274	0.144	0.146	0.077
2.010	1.891	4.200	1.527	0.241	0.663	0.052	13.585	3.793	5.899	0.818	0.384	0.203	0.149	0.079
2.000	1.882	4.120	2.367	0.241	0.876	0.057	21.059	3.793	7.794	0.897	0.663	0.352	0.145	0.077
2.020	1.901	4.220	3.195	0.241	1.136	0.054	28.425	3.793	10.107	0.850	0.916	0.482	0.147	0.077
2.000	1.882	4.180	3.432	0.241	1.373	0.055	30.534	3.793	12.215	0.866	0.916	0.487	0.146	0.078
1.990	1.873	4.200	0.556	0.904	0.195	0.091	4.947	14.227	1.735	1.432	0.161	0.086	0.640	0.342
2.000	1.882	4.260	1.077	0.904	0.428	0.096	9.582	14.227	3.808	1.511	0.289	0.153	0.636	0.338
1.990	1.873	4.280	1.574	0.904	0.662	0.096	14.004	14.227	5.890	1.511	0.406	0.217	0.636	0.340
2.010	1.891	4.260	2.604	0.904	0.896	0.098	23.167	14.227	7.972	1.542	0.760	0.402	0.634	0.335
2.010	1.891	4.220	2.840	0.904	1.130	0.100	25.267	14.227	10.053	1.574	0.761	0.402	0.633	0.334
2.020	1.901	4.280	3.432	0.904	1.364	0.095	30.534	14.227	12.135	1.495	0.920	0.484	0.637	0.335
2.020	1.901	4.220	0.545	3.892	0.239	0.387	4.849	61.253	2.126	6.091	0.136	0.072	2.758	1.451
2.010	1.891	4.240	1.065	3.892	0.507	0.387	9.475	61.253	4.511	6.091	0.248	0.131	2.758	1.458
1.990	1.873	4.260	1.584	3.892	0.761	0.406	14.093	61.253	6.770	6.390	0.366	0.196	2.743	1.465
2.000	1.882	4.220	2.597	3.892	1.007	0.387	23.105	61.253	8.959	6.091	0.707	0.376	2.758	1.466
2.010	1.891	4.240	2.727	3.892	1.261	0.387	24.262	61.253	11.219	6.091	0.652	0.345	2.758	1.458
2.030	1.910	4.240	3.117	3.892	1.529	0.443	27.731	61.253	13.603	6.972	0.706	0.370	2.714	1.421

coapetitive uptake: Cd vs Cu
soil: fen arable
oven dry cf: 0.958 Cd cf: 8.897 Cu cf: 15.738

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Cu ug/ml	final Cd ug/ml	final Cu ug/ml	init. Cd uM/l	init. Cu uM/l	final Cd uM/l	final Cu uM/l	Cadmium uptake uM	Cadmium soil up_take uM/g	Copper uptake uM	Copper soil up_take uM/g
2.030	1.945	6.940	0.544	0.241	0.007	0.043	4.840	3.793	0.067	0.677	0.239	0.123	0.156	0.080
2.030	1.945	7.140	1.041	0.241	0.012	0.039	9.262	3.793	0.107	0.614	0.458	0.235	0.159	0.082
2.000	1.916	7.180	1.527	0.241	0.014	0.039	13.585	3.793	0.125	0.614	0.673	0.351	0.159	0.083
2.000	1.916	7.160	2.367	0.241	0.026	0.039	21.059	3.793	0.231	0.614	1.041	0.544	0.159	0.083
1.990	1.906	7.160	3.195	0.241	0.026	0.036	28.425	3.793	0.231	0.567	1.410	0.739	0.161	0.085
2.000	1.916	7.160	3.432	0.241	0.034	0.032	30.534	3.793	0.302	0.504	1.512	0.789	0.164	0.086
2.000	1.916	7.160	0.556	0.904	0.015	0.066	4.947	14.227	0.133	1.039	0.241	0.126	0.659	0.344
2.000	1.916	7.180	1.077	0.904	0.007	0.068	9.582	14.227	0.062	1.070	0.476	0.248	0.658	0.343
2.000	1.916	7.300	1.574	0.904	0.013	0.071	14.004	14.227	0.116	1.117	0.694	0.362	0.655	0.342
2.010	1.926	7.260	2.604	0.904	0.011	0.064	23.167	14.227	0.098	1.007	1.153	0.599	0.661	0.343
2.010	1.926	7.100	2.840	0.904	0.033	0.068	25.267	14.227	0.294	1.070	1.249	0.648	0.658	0.342
2.000	1.916	7.280	3.432	0.904	0.040	0.068	30.534	14.227	0.356	1.070	1.509	0.788	0.658	0.343
2.000	1.916	7.020	0.545	3.892	0.004	0.166	4.849	61.253	0.036	2.613	0.241	0.126	2.932	1.530
2.020	1.935	7.140	1.065	3.892	0.010	0.184	9.475	61.253	0.089	2.896	0.469	0.243	2.918	1.508
2.000	1.916	7.120	1.584	3.892	0.018	0.166	14.093	61.253	0.160	2.613	0.697	0.364	2.932	1.530
2.010	1.926	7.120	2.597	3.892	0.024	0.092	23.105	61.253	0.214	1.448	1.145	0.594	2.990	1.553
2.020	1.935	7.100	2.727	3.892	0.030	0.129	24.262	61.253	0.267	2.030	1.200	0.620	2.961	1.530
2.010	1.926	7.100	3.117	3.892	0.038	0.148	27.731	61.253	0.338	2.329	1.370	0.711	2.946	1.530

coapetitive uptake: Cd vs Fe
soil: arkleston
oven dry cf: 0.907 Cd cf: 8.897 Fe cf: 17.905

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Fe ug/ml	final Cd ug/ml	final Fe ug/ml	init. Cd uM/l	init. Fe uM/l	final Cd uM/l	final Fe uM/l	Cadmium uptake uM	Cadmium soil up_take uM/g	Iron uptake uM	Iron soil up_take uM/g
2.000	1.814	4.300	0.550	0.060	0.040	0.360	4.893	1.074	0.356	6.446	0.227	0.125	-0.269	-0.148
1.990	1.805	4.560	1.090	0.060	0.090	0.420	9.698	1.074	0.801	7.520	0.445	0.246	-0.322	-0.179
2.000	1.814	4.800	1.620	0.060	0.120	0.420	14.413	1.074	1.068	7.520	0.667	0.368	-0.322	-0.178
1.990	1.805	4.500	2.160	0.060	0.230	0.420	19.217	1.074	2.046	7.520	0.859	0.476	-0.322	-0.179
2.000	1.814	4.460	2.720	0.060	0.320	0.360	24.199	1.074	2.847	6.446	1.068	0.589	-0.269	-0.148
2.000	1.814	4.550	3.280	0.060	0.380	0.360	29.181	1.074	3.381	6.446	1.290	0.711	-0.269	-0.148
1.990	1.805	4.480	0.560	0.620	0.040	0.640	4.982	11.101	0.356	11.459	0.231	0.128	-0.018	-0.010
2.000	1.814	4.580	1.100	0.620	0.090	0.560	9.786	11.101	0.801	10.027	0.449	0.248	0.054	0.030
1.990	1.805	4.780	1.580	0.620	0.120	0.560	14.057	11.101	1.068	10.027	0.649	0.360	0.054	0.030
2.030	1.841	4.540	2.160	0.620	0.210	0.530	19.217	11.101	1.868	9.490	0.867	0.471	0.081	0.044
2.000	1.814	4.560	2.800	0.620	0.260	0.500	24.911	11.101	2.313	8.953	1.130	0.623	0.107	0.059
2.000	1.814	4.520	2.960	0.620	0.330	0.670	26.335	11.101	2.936	11.996	1.170	0.645	-0.045	-0.025
2.000	1.814	4.660	0.570	2.710	0.030	0.500	5.071	48.523	0.267	8.953	0.240	0.132	1.979	1.091
2.000	1.814	4.560	1.120	2.710	0.100	0.550	9.964	48.523	0.890	9.848	0.454	0.250	1.934	1.066
1.990	1.805	4.580	1.630	2.710	0.180	0.600	14.502	48.523	1.601	10.743	0.645	0.357	1.889	1.047
1.990	1.805	4.440	2.320	2.710	0.260	0.550	20.641	48.523	2.313	9.848	0.916	0.508	1.934	1.071
2.000	1.814	4.480	2.880	2.710	0.340	0.600	25.623	48.523	3.025	10.743	1.130	0.623	1.889	1.041
2.000	1.814	4.500	4.160	2.710	0.410	0.650	37.011	48.523	3.648	11.638	1.668	0.920	1.844	1.017

coapetitive uptake: Cd vs Fe
soil: ahz
oven dry cf: 0.941 Cd cf: 8.897 Fe cf: 17.905

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Fe ug/ml	final Cd ug/ml	final Fe ug/ml	init. Cd uM/l	init. Fe uM/l	final Cd uM/l	final Fe uM/l	Cadmium uptake uM	Cadmium soil up_take uM/g	Iron uptake uM	Iron soil up_take uM/g
2.010	1.891	4.180	0.550	0.060	0.190	0.160	4.893	1.074	1.690	2.865	0.160	0.085	-0.090	-0.048
1.990	1.873	4.240	1.090	0.060	0.410	0.170	9.698	1.074	3.648	3.044	0.302	0.162	-0.098	-0.053
2.000	1.882	4.260	1.620	0.060	0.650	0.140	14.413	1.074	5.783	2.507	0.431	0.229	-0.072	-0.038
1.990	1.873	4.180	2.160	0.060	0.900	0.110	19.217	1.074	8.007	1.970	0.560	0.299	-0.045	-0.024
2.000	1.882	4.220	2.720	0.060	1.150	0.080	24.199	1.074	10.231	1.432	0.698	0.371	-0.018	-0.010
2.000	1.882	4.260	3.280	0.060	1.420	0.110	29.181	1.074	12.633	1.970	0.827	0.440	-0.045	-0.024
2.000	1.882	4.180	0.560	0.620	0.190	0.120	4.982	11.101	1.690	2.149	0.165	0.087	0.448	0.238
1.980	1.863	4.260	1.100	0.620	0.420	0.140	9.786	11.101	3.737	2.507	0.302	0.162	0.430	0.231
1.980	1.863	4.200	1.580	0.620	0.660	0.020	14.057	11.101	5.872	0.358	0.409	0.220	0.537	0.288
1.990	1.873	4.260	2.160	0.620	0.880	0.050	19.217	11.101	7.829	0.895	0.569	0.304	0.510	0.273
2.000	1.882	4.240	2.800	0.620	1.040	0.080	24.911	11.101	9.253	1.432	0.783	0.416	0.483	0.257
2.000	1.882	4.280	2.960	0.620	1.230	0.110	26.335	11.101	10.943	1.970	0.770	0.409	0.457	0.243
2.000	1.882	4.160	0.570	2.710	0.230	0.120	5.071	48.523	2.046	2.149	0.151	0.080	2.319	1.232
2.000	1.882	4.200	1.120	2.710	0.480	0.070	9.964	48.523	4.270	1.253	0.285	0.151	2.363	1.256
2.020	1.901	4.120	1.630	2.710	0.740	0.070	14.502	48.523	6.584	1.253	0.396	0.208	2.363	1.243
2.000	1.882	4.140	2.320	2.710	0.990	0.150	20.641	48.523	8.808	2.686	0.592	0.314	2.292	1.218
2.000	1.882	4.160	2.880	2.710	1.270	0.090	25.623	48.523	11.299	1.611	0.716	0.381	2.346	1.246
2.000	1.882	4.200	4.160	2.710	1.580	0.020	37.011	48.523	14.057	0.358	1.148	0.610	2.408	1.280

coapetitive uptake: Cd vs Fe.
soil: fen arable
oven dry cf: 0.958 Cd cf: 8.897 Fe cf: 17.905

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Fe ug/ml	final Cd ug/ml	final Fe ug/ml	init. Cd uM/l	init. Fe uM/l	final Cd uM/l	final Fe uM/l	Cadmium uptake uM	Cadmium soil up_take uM/g	Iron uptake uM	Iron soil up_take uM/g
1.990	1.906	6.940	0.550	0.060	0.005	0.280	4.893	1.074	0.047	5.013	0.242	0.127	-0.197	-0.103
2.000	1.916	7.060	1.090	0.060	0.011	0.280	9.698	1.074	0.098	5.013	0.480	0.251	-0.197	-0.103
1.980	1.897	7.060	1.620	0.060	0.021	0.310	14.413	1.074	0.187	5.551	0.711	0.375	-0.224	-0.118
2.000	1.916	7.060	2.160	0.060	0.029	0.280	19.217	1.074	0.258	5.013	0.948	0.495	-0.197	-0.103
1.990	1.906	7.080	2.720	0.060	0.034	0.310	24.199	1.074	0.302	5.551	1.195	0.627	-0.224	-0.117
2.010	1.926	7.040	3.280	0.060	0.048	0.310	29.181	1.074	0.427	5.551	1.438	0.747	-0.224	-0.116
1.990	1.906	7.340	0.560	0.620	0.090	0.310	4.982	11.101	0.801	5.551	0.209	0.110	0.278	0.146
1.990	1.906	7.320	1.100	0.620	0.027	0.250	9.786	11.101	0.240	4.476	0.477	0.250	0.331	0.174
2.000	1.916	7.340	1.580	0.620	0.024	0.250	14.057	11.101	0.214	4.476	0.692	0.361	0.331	0.173
2.010	1.926	7.380	2.160	0.620	0.027	0.310	19.217	11.101	0.240	5.551	0.949	0.493	0.278	0.144
2.000	1.916	7.300	2.800	0.620	0.027	0.280	24.911	11.101	0.240	5.013	1.234	0.644	0.304	0.159
1.990	1.906	7.340	2.960	0.620	0.024	0.250	26.335	11.101	0.214	4.476	1.306	0.685	0.331	0.174
1.990	1.906	7.120	0.570	2.710	0.022	1.100	5.071	48.523	0.196	19.696	0.244	0.128	1.441	0.756
2.000	1.916	7.220	1.120	2.710	0.016	0.900	9.964	48.523	0.142	16.115	0.491	0.256	1.620	0.846
2.020	1.935	7.340	1.630	2.710	0.022	1.050	14.502	48.523	0.196	18.800	0.715	0.370	1.486	0.768
2.000	1.916	7.280	2.320	2.710	0.021	1.000	20.641	48.523	0.187	17.905	1.023	0.534	1.531	0.799
2.000	1.916	7.300	2.880	2.710	0.021	1.000	25.623	48.523	0.187	17.905	1.272	0.664	1.531	0.799
2.000	1.916	7.200	4.160	2.710	0.054	1.150	37.011	48.523	0.480	20.591	1.827	0.953	1.397	0.729

competitive uptake: Cd vs Pb.
soil: arkleston
oven dry cf: 0.907 Cd cf: 8.897 Pb cf: 4.826

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init.Pb ug/ml	final Cd ug/ml	final Pb ug/ml	init. Cd uM/l	init. Pb uM/l	final Cd uM/l	final Pb uM/l	Cadmium uptake uM	Cadmium soil uptake uM/g	Lead uptake uM	Lead soil uptake uM/g
1.990	1.805	4.580	0.545	0.700	0.057	0.008	4.849	3.378	0.507	0.039	0.217	0.120	0.167	0.093
2.000	1.814	5.040	1.091	0.700	0.091	0.007	9.706	3.378	0.810	0.034	0.445	0.245	0.167	0.092
2.000	1.814	4.740	1.625	0.700	0.136	0.006	14.457	3.378	1.210	0.029	0.662	0.365	0.167	0.092
1.990	1.805	4.560	2.273	0.700	0.227	0.004	20.222	3.378	2.020	0.019	0.910	0.504	0.168	0.093
2.000	1.814	4.880	2.614	0.700	0.273	0.000	23.256	3.378	2.429	0.002	1.041	0.574	0.169	0.093
2.000	1.814	4.580	2.841	0.700	0.386	0.001	25.276	3.378	3.434	0.005	1.092	0.602	0.169	0.093
1.990	1.805	5.480	0.557	2.360	0.013	0.009	4.956	11.389	0.116	0.043	0.242	0.134	0.567	0.314
2.000	1.814	4.680	1.091	2.360	0.077	0.015	9.706	11.389	0.685	0.072	0.451	0.249	0.566	0.312
2.000	1.814	4.680	1.636	2.360	0.141	0.017	14.555	11.389	1.254	0.082	0.665	0.367	0.565	0.312
1.990	1.805	4.620	2.273	2.360	0.192	0.016	20.222	11.389	1.708	0.077	0.926	0.513	0.566	0.313
1.990	1.805	4.660	2.841	2.360	0.269	0.017	25.276	11.389	2.393	0.082	1.144	0.634	0.565	0.313
1.990	1.805	4.600	3.182	2.360	0.372	0.017	28.310	11.389	3.310	0.082	1.250	0.693	0.565	0.313
2.000	1.814	4.740	0.566	10.860	0.061	0.064	5.036	52.411	0.543	0.309	0.225	0.124	2.605	1.436
2.010	1.823	4.680	1.121	10.860	0.131	0.070	9.973	52.411	1.165	0.338	0.440	0.242	2.604	1.428
1.990	1.805	4.620	1.656	10.860	0.202	0.068	14.733	52.411	1.797	0.328	0.647	0.358	2.604	1.443
2.000	1.814	4.540	2.140	10.860	0.293	0.078	19.039	52.411	2.607	0.376	0.822	0.453	2.602	1.434
2.000	1.814	4.620	2.620	10.860	0.323	0.060	23.310	52.411	2.874	0.290	1.022	0.563	2.606	1.437
2.000	1.814	4.540	3.100	10.860	0.454	0.078	27.580	52.411	4.039	0.376	1.177	0.649	2.602	1.434

competitive uptake: Cd vs Pb.
soil: ahz
oven dry cf: 0.941 Cd cf: 8.897 Pb cf: 4.826

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init.Pb ug/ml	final Cd ug/ml	final Pb ug/ml	init. Cd uM/l	init.Pb uM/l	final Cd uM/l	final Pb uM/l	Cadmium uptake uM	Cadmium soil uptake uM/g	Lead uptake uM	Lead soil uptake uM/g
2.010	1.891	4.180	0.545	0.700	0.216	0.012	4.849	3.378	1.922	0.058	0.146	0.077	0.166	0.088
2.020	1.901	4.280	1.091	0.700	0.443	0.012	9.706	3.378	3.941	0.058	0.288	0.152	0.166	0.087
1.990	1.873	4.260	1.625	0.700	0.682	0.011	14.457	3.378	6.068	0.053	0.419	0.224	0.166	0.089
2.000	1.882	4.240	2.273	0.700	0.909	0.017	20.222	3.378	8.087	0.082	0.607	0.322	0.165	0.088
2.000	1.882	4.280	2.614	0.700	1.159	0.013	23.256	3.378	10.311	0.063	0.647	0.344	0.166	0.088
1.990	1.873	4.280	2.841	0.700	1.454	0.014	25.276	3.378	12.936	0.068	0.617	0.329	0.166	0.088
2.000	1.882	4.300	0.557	2.360	0.179	0.088	4.956	11.389	1.593	0.425	0.168	0.089	0.548	0.291
2.000	1.882	4.340	1.091	2.360	0.410	0.085	9.706	11.389	3.648	0.410	0.303	0.161	0.549	0.292
2.010	1.891	4.320	1.636	2.360	0.667	0.092	14.555	11.389	5.934	0.444	0.431	0.228	0.547	0.289
1.990	1.873	4.250	2.273	2.360	0.897	0.110	20.222	11.389	7.980	0.531	0.612	0.327	0.543	0.290
2.010	1.891	4.300	2.841	2.360	1.141	0.097	25.276	11.389	10.151	0.468	0.756	0.400	0.546	0.289
1.990	1.873	4.700	3.182	2.360	1.256	0.069	28.310	11.389	11.174	0.333	0.857	0.458	0.553	0.295
1.990	1.873	4.300	0.566	10.860	0.263	0.548	5.036	52.411	2.340	2.645	0.135	0.072	2.488	1.329
2.000	1.882	4.300	1.121	10.860	0.505	0.439	9.973	52.411	4.493	2.119	0.274	0.146	2.515	1.336
2.020	1.901	4.200	1.656	10.860	0.767	0.414	14.733	52.411	6.824	1.998	0.395	0.208	2.521	1.326
2.000	1.882	4.250	2.140	10.860	1.030	0.458	19.039	52.411	9.164	2.210	0.494	0.262	2.510	1.334
2.020	1.901	4.280	2.620	10.860	1.343	0.583	23.310	52.411	11.948	2.814	0.568	0.299	2.480	1.305
1.990	1.873	4.200	3.100	10.860	1.626	0.415	27.580	52.411	14.466	2.003	0.656	0.350	2.520	1.346

competitive uptake: Cd vs Pb.
soil: fen arable
oven dry cf: 0.958 Cd cf: 8.897 Pb cf: 4.826

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init.Pb ug/ml	final Cd ug/ml	final Pb ug/ml	init. Cd uM/l	init. Pb uM/l	final Cd uM/l	final Pb uM/l	Cadmium uptake uM	Cadmium soil uptake uM/g	Lead uptake uM	Lead soil uptake uM/g
1.990	1.906	7.280	0.545	0.700	0.004	nd	4.849	3.378	0.036	0.000	0.241	0.126	0.169	0.089
2.000	1.916	7.220	1.091	0.700	0.006	nd	9.706	3.378	0.053	0.000	0.483	0.252	0.169	0.088
2.010	1.926	7.360	1.625	0.700	0.021	nd	14.457	3.378	0.187	0.000	0.714	0.371	0.169	0.088
1.990	1.906	7.280	2.273	0.700	0.024	nd	20.222	3.378	0.214	0.000	1.000	0.525	0.169	0.089
2.010	1.926	7.300	2.614	0.700	0.031	nd	23.256	3.378	0.276	0.000	1.149	0.597	0.169	0.088
1.990	1.906	7.320	2.841	0.700	0.021	nd	25.276	3.378	0.187	0.000	1.254	0.658	0.169	0.089
1.990	1.906	7.280	0.557	2.360	0.022	0.004	4.956	11.389	0.196	0.019	0.238	0.125	0.569	0.298
2.010	1.926	7.160	1.091	2.360	0.016	0.004	9.706	11.389	0.142	0.019	0.478	0.248	0.569	0.295
2.000	1.916	7.340	1.636	2.360	0.016	0.004	14.555	11.389	0.142	0.019	0.721	0.376	0.569	0.297
2.000	1.916	7.280	2.273	2.360	0.024	0.004	20.222	11.389	0.214	0.019	1.000	0.522	0.569	0.297
1.990	1.906	7.220	2.841	2.360	0.024	0.003	25.276	11.389	0.214	0.014	1.253	0.657	0.569	0.298
2.000	1.916	7.340	3.182	2.360	0.036	0.003	28.310	11.389	0.320	0.014	1.399	0.730	0.569	0.297
2.000	1.916	7.380	0.566	10.860	0.002	0.010	5.036	52.411	0.018	0.048	0.251	0.131	2.618	1.366
1.990	1.906	7.300	1.121	10.860	0.008	0.010	9.973	52.411	0.071	0.048	0.495	0.260	2.618	1.373
2.010	1.926	7.300	1.656	10.860	0.005	0.015	14.733	52.411	0.044	0.072	0.734	0.381	2.617	1.359
1.990	1.906	7.300	2.140	10.860	0.020	0.016	19.039	52.411	0.178	0.077	0.943	0.495	2.617	1.373
2.010	1.926	7.300	2.620	10.860	0.026	0.016	23.310	52.411	0.231	0.077	1.154	0.599	2.617	1.359
2.030	1.945	7.320	3.100	10.860	0.029	0.012	27.580	52.411	0.258	0.058	1.366	0.702	2.618	1.346

coapetitive uptake: Cd vs Zn
soil: arkleston
oven dry cf: 0.907 Cd cf: 8.897 Zn cf: 15.295

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Zn ug/ml	final Cd ug/ml	final Zn ug/ml	init. Cd uM/l	init. Zn uM/l	final Cd uM/l	final Zn uM/l	Cadmium uptake uM	Cadmium soil uptake uM/g	Zinc uptake uM	Zinc soil uptake uM/g
2.000	1.814	4.440	0.519	0.324	0.033	0.225	4.617	4.956	0.294	3.441	0.216	0.119	0.076	0.042
2.000	1.814	4.460	1.038	0.324	0.092	0.225	9.235	4.956	0.819	3.441	0.421	0.232	0.076	0.042
1.990	1.805	4.460	1.490	0.324	0.159	0.231	13.256	4.956	1.415	3.533	0.592	0.328	0.071	0.039
2.010	1.823	4.380	1.925	0.324	0.226	0.243	17.126	4.956	2.011	3.717	0.756	0.415	0.062	0.034
2.020	1.832	4.360	2.510	0.324	0.284	0.248	22.331	4.956	2.527	3.793	0.990	0.540	0.058	0.032
2.010	1.823	4.440	3.096	0.324	0.360	0.248	27.544	4.956	3.203	3.793	1.217	0.668	0.058	0.032
2.000	1.814	4.460	0.519	0.983	0.044	0.359	4.617	15.035	0.391	5.491	0.211	0.116	0.477	0.263
2.000	1.814	4.620	1.029	0.983	0.096	0.331	9.155	15.035	0.854	5.063	0.415	0.229	0.499	0.275
2.020	1.832	4.460	1.506	0.983	0.158	0.352	13.399	15.035	1.406	5.384	0.600	0.327	0.483	0.263
2.020	1.832	4.540	1.841	0.983	0.210	0.331	16.379	15.035	1.868	5.063	0.726	0.396	0.499	0.272
2.000	1.814	4.480	2.510	0.983	0.307	0.372	22.331	15.035	2.731	5.690	0.980	0.540	0.467	0.258
1.990	1.805	4.480	3.012	0.983	0.386	0.372	26.797	15.035	3.434	5.690	1.168	0.647	0.467	0.259
2.010	1.823	4.620	0.544	3.862	0.053	1.242	4.840	59.070	0.472	18.997	0.218	0.120	2.004	1.099
1.990	1.805	4.540	1.044	3.862	0.123	1.180	9.288	59.070	1.094	18.048	0.410	0.227	2.051	1.136
1.990	1.805	4.460	1.553	3.862	0.184	1.161	13.817	59.070	1.637	17.758	0.609	0.337	2.066	1.144
2.000	1.814	4.460	2.193	3.862	0.281	1.230	19.511	59.070	2.500	18.813	0.851	0.469	2.013	1.110
2.010	1.823	4.500	2.544	3.862	0.333	1.155	22.633	59.070	2.963	17.666	0.984	0.539	2.070	1.136
2.000	1.814	4.620	3.070	3.862	0.403	1.137	27.313	59.070	3.585	17.391	1.186	0.654	2.084	1.149

coapetitive uptake: Cd vs Zn
soil: ahz
oven dry cf: 0.941 Cd cf: 8.897 Zn cf: 15.295

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Zn ug/ml	final Cd ug/ml	final Zn ug/ml	init. Cd uM/l	init. Zn uM/l	final Cd uM/l	final Zn uM/l	Cadmium uptake uM	Cadmium soil uptake uM/g	Zinc uptake uM	Zinc soil uptake uM/g
2.010	1.891	4.160	0.519	0.324	0.192	1.965	4.617	4.956	1.708	30.055	0.145	0.077	-1.255	-0.664
2.000	1.882	4.180	1.038	0.324	0.410	2.139	9.235	4.956	3.648	32.716	0.279	0.148	-1.388	-0.738
1.990	1.873	4.200	1.490	0.324	0.619	1.965	13.256	4.956	5.507	30.055	0.387	0.207	-1.255	-0.670
2.020	1.901	4.220	1.925	0.324	0.853	2.023	17.126	4.956	7.589	30.942	0.477	0.251	-1.299	-0.684
2.000	1.882	4.220	2.510	0.324	1.071	1.965	22.331	4.956	9.528	30.055	0.640	0.340	-1.255	-0.667
1.990	1.873	4.240	3.096	0.324	1.389	1.965	27.544	4.956	12.358	30.055	0.759	0.406	-1.255	-0.670
1.990	1.873	4.240	0.519	0.983	0.193	2.000	4.617	15.035	1.717	30.590	0.145	0.077	-0.778	-0.415
2.000	1.882	4.260	1.029	0.983	0.412	2.000	9.155	15.035	3.665	30.590	0.274	0.146	-0.778	-0.413
2.000	1.882	4.240	1.506	0.983	0.640	2.069	13.399	15.035	5.694	31.646	0.385	0.205	-0.831	-0.441
2.000	1.882	4.280	1.841	0.983	0.877	2.138	16.379	15.035	7.802	32.701	0.429	0.228	-0.883	-0.469
2.000	1.882	4.220	2.510	0.983	1.140	2.483	22.331	15.035	10.142	37.978	0.609	0.324	-1.147	-0.610
2.010	1.891	4.220	3.012	0.983	1.386	2.276	26.797	15.035	12.331	34.812	0.723	0.382	-0.989	-0.523
2.000	1.882	4.280	0.544	3.862	0.210	4.658	4.840	59.070	1.868	71.245	0.149	0.079	-0.609	-0.323
2.000	1.882	4.280	1.044	3.862	0.447	4.720	9.288	59.070	3.977	72.193	0.266	0.141	-0.656	-0.349
2.000	1.882	4.280	1.553	3.862	0.667	3.851	13.817	59.070	5.934	58.902	0.394	0.209	0.008	0.004
1.990	1.873	4.340	2.193	3.862	0.938	4.969	19.511	59.070	8.345	76.002	0.558	0.298	-0.847	-0.452
1.990	1.873	4.360	2.544	3.862	1.158	5.093	22.633	59.070	10.302	77.898	0.617	0.329	-0.941	-0.503
2.010	1.891	4.380	3.070	3.862	1.386	4.099	27.313	59.070	12.331	62.695	0.749	0.396	-0.181	-0.096

coapetitive uptake: Cd vs Zn
soil: fen arable
oven dry cf: 0.958 Cd cf: 8.897 Zn cf: 15.295

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cd ug/ml	init. Zn ug/ml	final Cd ug/ml	final Zn ug/ml	init. Cd uM/l	init. Zn uM/l	final Cd uM/l	final Zn uM/l	Cadmium uptake uM	Cadmium soil uptake uM/g	Zinc uptake uM	Zinc soil uptake uM/g
2.000	1.916	7.160	0.519	0.324	0.022	0.001	4.617	4.956	0.196	0.012	0.221	0.115	0.247	0.129
1.990	1.906	7.100	1.038	0.324	0.009	0.001	9.235	4.956	0.080	0.009	0.458	0.240	0.247	0.130
2.000	1.916	7.320	1.490	0.324	0.011	0.001	13.256	4.956	0.098	0.011	0.658	0.343	0.247	0.129
2.010	1.926	7.320	1.925	0.324	0.017	0.017	17.126	4.956	0.151	0.262	0.849	0.441	0.235	0.122
2.000	1.916	7.260	2.510	0.324	0.026	0.001	22.331	4.956	0.231	0.008	1.105	0.577	0.247	0.129
1.990	1.906	7.300	3.096	0.324	0.027	0.002	27.544	4.956	0.240	0.031	1.365	0.716	0.246	0.129
1.990	1.906	7.160	0.519	0.983	0.014	0.002	4.617	15.035	0.125	0.031	0.225	0.118	0.750	0.394
2.000	1.916	7.300	1.029	0.983	0.013	0.004	9.155	15.035	0.116	0.061	0.452	0.236	0.749	0.391
2.000	1.916	7.260	1.506	0.983	0.018	0.003	13.399	15.035	0.160	0.046	0.662	0.345	0.749	0.391
2.020	1.935	7.080	1.841	0.983	0.028	0.004	16.379	15.035	0.249	0.061	0.806	0.417	0.749	0.387
1.990	1.906	7.220	2.510	0.983	0.032	0.002	22.331	15.035	0.285	0.031	1.102	0.578	0.750	0.394
1.990	1.906	7.160	3.012	0.983	0.043	0.002	26.797	15.035	0.383	0.031	1.321	0.693	0.750	0.394
2.000	1.916	7.140	0.544	3.862	0.045	0.062	4.840	59.070	0.400	0.948	0.222	0.116	2.906	1.517
1.990	1.906	7.120	1.044	3.862	0.014	0.062	9.288	59.070	0.125	0.948	0.458	0.240	2.906	1.524
2.010	1.926	7.140	1.553	3.862	0.022	0.062	13.817	59.070	0.196	0.948	0.681	0.354	2.906	1.509
1.990	1.906	7.180	2.193	3.862	0.029	0.062	19.511	59.070	0.258	0.948	0.963	0.505	2.906	1.524
2.000	1.916	7.060	2.544	3.862	0.039	0.062	22.633	59.070	0.347	0.948	1.114	0.582	2.906	1.517
2.000	1.916	7.120	3.070	3.862	0.050	0.062	27.313	59.070	0.445	0.948	1.343	0.701	2.906	1.517

coapetitive uptake: Cu vs Cd
soil: ahz
oven dry cf: 0.941 Cu cf: 15.738 Cd cf: 8.897

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Cd ug/ml	final Cu ug/ml	final Cd ug/ml	init.Cu uM/l	init.Cd uM/l	final Cu uM/l	final Cd uM/l	Copper uptake uM	Copper soil uptake uM/g	Cadmium uptake uM	Cadmium soil uptake uM/g
1.990	1.873	4.284	0.560	0.340	0.057	0.160	8.813	3.203	0.899	1.423	0.396	0.211	0.089	0.048
2.020	1.901	4.320	0.380	0.700	0.066	0.310	5.980	6.228	1.040	2.758	0.247	0.130	0.173	0.091
2.000	1.882	4.300	0.560	1.010	0.078	0.480	8.813	8.986	1.226	4.270	0.379	0.202	0.236	0.125
1.990	1.873	4.320	0.740	1.300	0.085	0.640	11.646	11.566	1.338	5.694	0.515	0.275	0.294	0.157
2.000	1.882	4.240	0.940	1.610	0.100	0.800	14.794	14.324	1.571	7.117	0.661	0.351	0.360	0.191
1.990	1.873	4.240	1.120	1.890	0.109	1.000	17.627	16.815	1.712	8.897	0.796	0.425	0.396	0.211
2.000	1.882	4.260	1.320	3.480	0.123	1.190	20.774	30.961	1.942	10.587	0.942	0.500	1.019	0.541
1.990	1.873	4.260	1.490	4.420	0.137	1.360	23.450	39.324	2.148	12.100	1.065	0.569	1.361	0.727
2.010	1.891	4.280	1.670	4.560	0.145	1.480	26.283	40.569	2.285	13.167	1.200	0.634	1.370	0.724
2.000	1.882	4.280	1.860	3.620	0.174	1.676	29.273	32.206	2.732	14.911	1.327	0.705	0.865	0.459
2.000	1.882	4.300	7.000	10.870	0.800	6.380	110.167	96.708	12.590	56.762	4.879	2.592	1.997	1.061
2.010	1.891	4.240	11.860	20.940	3.100	15.000	186.654	186.299	48.788	133.452	6.893	3.645	2.642	1.397
2.000	1.882	4.220	21.600	29.710	6.600	26.090	339.943	264.324	103.872	232.117	11.804	6.272	1.610	0.856

coapetitive uptake: Cu vs Cd.
soil: fen arable
oven dry cf: 0.958 Cu cf: 15.738 Cd cf: 8.897

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Cd ug/ml	final Cu ug/ml	final Cd ug/ml	init.Cu uM/l	init.Cd uM/l	final Cu uM/l	final Cd uM/l	Copper uptake uM	Copper soil uptake uM/g	Cadmium uptake uM	Cadmium soil uptake uM/g
1.990	1.906	7.380	0.560	0.360	0.038	0.007	8.813	3.203	0.604	0.063	0.410	0.215	0.157	0.082
2.010	1.926	7.340	0.380	0.700	0.043	0.006	5.980	6.228	0.670	0.055	0.266	0.138	0.309	0.160
2.010	1.926	7.380	0.560	1.010	0.049	0.009	8.813	8.986	0.777	0.080	0.402	0.209	0.445	0.231
2.000	1.916	7.380	0.740	1.300	0.054	0.012	11.646	11.566	0.855	0.107	0.540	0.282	0.573	0.299
2.000	1.916	7.300	0.940	1.610	0.063	0.016	14.794	14.324	0.998	0.145	0.690	0.360	0.709	0.370
1.990	1.906	7.300	1.120	1.890	0.069	0.018	17.627	16.815	1.081	0.161	0.827	0.434	0.833	0.437
2.020	1.935	7.240	1.320	3.480	0.080	0.043	20.774	30.961	1.254	0.386	0.976	0.504	1.529	0.790
2.000	1.916	7.220	1.490	4.420	0.088	0.058	23.450	39.324	1.382	0.516	1.103	0.576	1.940	1.013
2.000	1.916	7.380	1.670	4.560	0.089	0.051	26.283	40.569	1.399	0.451	1.244	0.649	2.006	1.047
2.000	1.916	7.320	1.860	3.620	0.088	0.058	29.273	32.206	1.379	0.516	1.395	0.728	1.585	0.827
2.010	1.926	6.960	7.000	10.870	0.213	0.210	110.167	96.708	3.351	1.869	5.341	2.774	4.742	2.463
1.990	1.906	6.860	11.860	20.940	0.350	0.515	186.654	186.299	5.505	4.577	9.057	4.751	9.086	4.766
1.990	1.906	6.700	21.600	29.710	0.487	0.935	339.943	264.324	7.660	8.317	16.614	8.715	12.800	6.714

coapetitive uptake: Cu vs Cd
soil: arkleston
oven dry cf: 0.907 Cu cf: 15.738 Cd cf: 8.897

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Cd ug/ml	final Cu ug/ml	final Cd ug/ml	init.Cu uM/l	init.Cd uM/l	final Cu uM/l	final Cd uM/l	Copper uptake uM	Copper soil uptake uM/g	Cadmium uptake uM	Cadmium soil uptake uM/g
2.000	1.814	4.520	0.560	0.360	0.026	0.050	8.813	3.203	0.404	0.445	0.420	0.232	0.138	0.076
2.000	1.814	4.580	0.380	0.700	0.029	0.080	5.980	6.228	0.452	0.712	0.276	0.152	0.276	0.152
2.000	1.814	4.544	0.560	1.010	0.029	0.130	8.813	8.986	0.452	1.157	0.418	0.230	0.391	0.216
2.020	1.832	4.560	0.740	1.300	0.035	0.180	11.646	11.566	0.554	1.601	0.555	0.303	0.498	0.272
2.020	1.832	4.460	0.940	1.610	0.035	0.220	14.794	14.324	0.552	1.957	0.712	0.389	0.618	0.337
2.000	1.814	4.520	1.120	1.890	0.037	0.290	17.627	16.815	0.576	2.580	0.853	0.470	0.712	0.392
2.000	1.814	4.520	1.320	3.480	0.043	0.350	20.774	30.961	0.680	3.114	1.005	0.554	1.392	0.768
1.990	1.805	4.540	1.490	4.420	0.051	0.400	23.450	39.324	0.801	3.559	1.132	0.627	1.788	0.991
1.990	1.805	4.540	1.670	4.560	0.054	0.470	26.283	40.569	0.844	4.181	1.272	0.705	1.819	1.008
2.010	1.823	4.540	1.860	3.620	0.057	0.510	29.273	32.206	0.900	4.537	1.419	0.778	1.383	0.759
2.000	1.814	4.420	7.000	10.870	0.167	3.980	110.167	96.708	2.624	35.409	5.377	2.964	3.065	1.690
2.000	1.814	4.380	11.860	20.940	0.517	8.840	186.654	186.299	8.132	78.648	8.926	4.921	5.383	2.967
2.000	1.814	4.340	21.600	29.710	1.083	14.780	339.943	264.324	17.049	131.495	16.145	8.900	6.641	3.661

competitive uptake: Cu vs Fe
soil: ahz
oven dry cf: 0.941 Cu cf: 15.738 Fe cf: 17.905

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Fe ug/ml	final Cu ug/ml	final Fe ug/ml	init.Cu uM/l	init.Fe uM/l	final Cu uM/l	final Fe uM/l	Copper uptake uM	Copper soil up_take uM/g	Iron uptake uM	Iron soil up_take uM/g
2.000	1.882	4.380	0.210	0.100	0.036	0.015	3.305	1.791	0.567	0.270	0.137	0.073	0.076	0.040
1.990	1.873	4.340	0.400	0.240	0.043	0.013	6.295	4.297	0.677	0.224	0.281	0.150	0.204	0.109
2.010	1.891	4.340	0.600	0.310	0.056	0.013	9.443	5.551	0.881	0.233	0.428	0.226	0.266	0.141
2.000	1.882	4.280	0.770	0.320	0.070	0.013	12.118	5.730	1.102	0.224	0.551	0.293	0.275	0.146
2.040	1.920	4.260	0.960	0.480	0.077	0.014	15.109	8.594	1.212	0.256	0.695	0.362	0.417	0.217
2.030	1.910	4.260	1.150	0.580	0.091	0.012	18.099	10.385	1.432	0.217	0.833	0.436	0.508	0.266
1.990	1.873	4.260	1.360	0.640	0.102	0.011	21.404	11.459	1.605	0.193	0.990	0.529	0.563	0.301
2.010	1.891	4.240	1.540	0.740	0.107	0.009	24.237	13.250	1.684	0.158	1.128	0.596	0.655	0.346
2.010	1.891	4.240	1.730	0.990	0.135	0.012	27.227	17.726	2.125	0.220	1.255	0.664	0.875	0.463
2.010	1.891	4.240	1.940	1.280	0.140	0.017	30.532	22.919	2.203	0.301	1.416	0.749	1.131	0.598
2.000	1.882	4.080	7.120	7.690	1.170	0.016	112.055	137.690	18.414	0.295	4.682	2.488	6.870	3.650
2.000	1.882	3.960	13.650	11.860	3.900	0.020	214.825	212.355	61.379	0.355	7.672	4.077	10.600	5.632
2.000	1.882	3.760	19.810	15.710	8.480	0.023	311.772	281.289	133.459	0.408	8.916	4.737	14.044	7.462

competitive uptake: Cu vs Fe
soil: fen arable
oven dry cf: 0.958 Cu cf: 15.738 Fe cf: 17.905

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Fe ug/ml	final Cu ug/ml	final Fe ug/ml	init.Cu uM/l	init.Fe uM/l	final Cu uM/l	final Fe uM/l	Copper uptake uM	Copper soil up_take uM/g	Iron uptake uM	Iron soil up_take uM/g
1.990	1.906	7.280	0.210	0.100	0.028	0.220	3.305	1.791	0.434	3.939	0.144	0.075	-0.107	-0.056
2.000	1.916	7.220	0.400	0.240	0.034	0.260	6.295	4.297	0.538	4.655	0.288	0.150	-0.018	-0.009
1.990	1.906	7.180	0.600	0.310	0.041	0.350	9.443	5.551	0.639	6.267	0.440	0.231	-0.036	-0.019
2.000	1.916	7.240	0.770	0.320	0.048	0.260	12.118	5.730	0.755	4.655	0.568	0.297	0.054	0.028
2.000	1.916	7.220	0.960	0.480	0.050	0.260	15.109	8.594	0.788	4.655	0.716	0.374	0.197	0.103
1.980	1.897	6.880	1.150	0.580	0.070	0.290	18.099	10.385	1.095	5.192	0.850	0.448	0.260	0.137
2.020	1.935	6.980	1.360	0.640	0.069	0.350	21.404	11.459	1.089	6.267	1.016	0.525	0.260	0.134
2.010	1.926	7.060	1.540	0.740	0.070	0.320	24.237	13.250	1.100	5.730	1.157	0.601	0.376	0.195
2.010	1.926	7.060	1.730	0.990	0.072	0.380	27.227	17.726	1.136	6.804	1.305	0.677	0.546	0.284
2.010	1.926	6.980	1.940	1.280	0.076	0.420	30.532	22.919	1.188	7.520	1.467	0.762	0.770	0.400
2.000	1.916	4.200	7.120	7.690	0.167	0.450	112.055	137.690	2.630	8.057	5.471	2.856	6.482	3.383
2.000	1.916	6.940	13.650	11.860	0.289	0.580	214.825	212.355	4.540	10.385	10.514	5.488	10.098	5.271
2.010	1.926	6.780	19.810	15.710	0.404	0.510	311.772	281.289	6.355	9.132	15.271	7.931	13.608	7.067

competitive uptake: Cu vs Fe
soil: arkleston
oven dry cf: 0.907 Cu cf: 15.738 Fe cf: 17.905

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Fe ug/ml	final Cu ug/ml	final Fe ug/ml	init.Cu uM/l	init.Fe uM/l	final Cu uM/l	final Fe uM/l	Copper uptake uM	Copper soil up_take uM/g	Iron uptake uM	Iron soil up_take uM/g
2.020	1.832	4.680	0.210	0.100	0.013	0.300	3.305	1.791	0.201	5.372	0.155	0.085	-0.179	-0.098
2.020	1.832	4.600	0.400	0.240	0.019	0.330	6.295	4.297	0.301	5.909	0.300	0.164	-0.081	-0.044
1.990	1.805	4.720	0.600	0.310	0.018	0.330	9.443	5.551	0.283	5.909	0.458	0.254	-0.018	-0.010
2.000	1.814	4.600	0.770	0.320	0.020	0.390	12.118	5.730	0.315	6.983	0.590	0.325	-0.063	-0.035
2.020	1.832	4.620	0.960	0.480	0.023	0.330	15.109	8.594	0.368	5.909	0.737	0.402	0.134	0.073
2.000	1.814	4.580	1.150	0.580	0.026	0.360	18.099	10.385	0.411	6.446	0.884	0.488	0.197	0.109
1.990	1.805	4.540	1.360	0.640	0.033	0.360	21.404	11.459	0.519	6.446	1.044	0.579	0.251	0.139
1.990	1.805	4.620	1.540	0.740	0.034	0.450	24.237	13.250	0.538	8.057	1.185	0.656	0.260	0.144
2.000	1.814	4.640	1.730	0.990	0.034	0.300	27.227	17.726	0.532	5.372	1.335	0.736	0.618	0.341
2.040	1.850	4.600	1.940	1.280	0.037	0.510	30.532	22.919	0.581	9.132	1.498	0.809	0.689	0.373
1.990	1.805	4.560	7.120	7.690	0.160	0.210	112.055	137.690	2.518	3.760	5.477	3.034	6.697	3.710
2.000	1.814	5.620	13.650	11.860	0.140	0.580	214.825	212.355	2.203	10.385	10.631	5.861	10.098	5.567
1.990	1.805	4.140	19.810	15.710	2.230	0.090	311.772	281.289	35.096	1.611	13.834	7.664	13.984	7.748

coapetitive uptake: Cu vs Pb
soil: ahz
oven dry cf: 0.941 Cu cf: 15.738 Pb cf: 4.826

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Pb ug/ml	final Cu ug/ml	final Pb ug/ml	init.Cu uM/l	init.Pb uM/l	final Cu uM/l	final Pb uM/l	Copper uptake uM	Copper soil up_take uM/g	Lead uptake uM	Lead soil up_take uM/g
2.070	1.948	4.340	0.190	0.530	0.032	0.033	2.990	2.558	0.500	0.161	0.124	0.064	0.120	0.062
1.990	1.873	4.320	0.420	1.200	0.039	0.054	6.610	5.791	0.611	0.259	0.300	0.160	0.277	0.148
1.990	1.873	4.400	0.620	1.330	0.054	0.063	9.758	6.419	0.851	0.305	0.445	0.238	0.306	0.163
1.990	1.873	4.320	0.810	2.400	0.066	0.069	12.748	11.582	1.040	0.333	0.585	0.313	0.562	0.300
1.990	1.873	4.240	1.020	2.670	0.079	0.096	16.053	12.885	1.248	0.462	0.740	0.395	0.621	0.332
1.990	1.873	4.280	1.241	3.600	0.085	0.106	19.531	17.374	1.346	0.512	0.909	0.486	0.843	0.450
2.020	1.901	4.320	1.390	4.130	0.101	0.135	21.876	19.931	1.590	0.651	1.014	0.534	0.964	0.507
1.990	1.873	4.280	1.600	4.800	0.123	0.132	25.181	23.165	1.936	0.637	1.162	0.621	1.126	0.602
2.020	1.901	4.280	1.830	5.330	0.146	0.146	28.801	25.723	2.299	0.705	1.325	0.697	1.251	0.658
1.990	1.873	4.280	2.010	6.000	0.150	0.158	31.634	28.956	2.361	0.763	1.464	0.782	1.410	0.753
2.000	1.882	7.220	7.720	20.400	1.072	2.070	121.498	98.451	16.871	9.990	5.231	2.780	4.423	2.350
1.990	1.873	4.160	13.710	40.000	5.290	5.450	215.770	193.041	83.255	26.302	6.626	3.538	8.337	4.452
2.010	1.891	4.100	19.880	60.000	8.540	12.950	312.874	289.561	134.404	62.497	8.924	4.718	11.353	6.003

coapetitive uptake: Cu vs Pb
soil: fen arable
oven dry cf: 0.958 Cu cf: 15.738 Pb cf: 4.826

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Pb ug/ml	final Cu ug/ml	final Pb ug/ml	init.Cu uM/l	init.Pb uM/l	final Cu uM/l	final Pb uM/l	Copper uptake uM	Copper soil up_take uM/g	Lead uptake uM	Lead soil up_take uM/g
1.990	1.906	7.360	0.190	0.530	0.028	0.001	2.990	2.558	0.442	0.004	0.127	0.067	0.128	0.067
1.980	1.897	7.327	0.420	1.200	0.035	0.007	6.610	5.791	0.551	0.033	0.303	0.160	0.288	0.152
1.990	1.906	7.360	0.620	1.330	0.041	0.001	9.758	6.419	0.637	0.007	0.456	0.239	0.321	0.168
2.000	1.916	7.320	0.810	2.400	0.046	0.006	12.748	11.582	0.719	0.028	0.601	0.314	0.578	0.302
2.000	1.916	7.240	1.020	2.670	0.054	0.002	16.053	12.885	0.844	0.012	0.760	0.397	0.644	0.336
1.990	1.906	7.280	1.241	3.600	0.058	0.020	19.531	17.374	0.910	0.095	0.931	0.488	0.864	0.453
2.010	1.926	7.280	1.390	4.130	0.064	0.023	21.876	19.931	1.004	0.109	1.044	0.542	0.991	0.515
1.990	1.906	7.300	1.600	4.800	0.067	0.006	25.181	23.165	1.058	0.030	1.206	0.633	1.157	0.607
2.000	1.916	7.280	1.830	5.330	0.074	0.006	28.801	25.723	1.165	0.031	1.382	0.721	1.285	0.670
1.990	1.906	7.280	2.010	6.000	0.083	0.015	31.634	28.956	1.308	0.072	1.516	0.795	1.444	0.758
2.000	1.916	7.220	7.720	20.400	0.210	0.031	121.498	98.451	3.305	0.148	5.910	3.084	4.915	2.565
1.990	1.906	7.040	13.710	40.000	0.330	0.071	215.770	193.041	5.194	0.342	10.529	5.523	9.635	5.054
2.000	1.916	6.880	19.880	60.000	0.440	0.128	312.874	289.561	6.925	0.619	15.297	7.984	14.447	7.540

coapetitive uptake: Cu vs Pb
soil: arkleston
oven dry cf: 0.907 Cu cf: 15.738 Pb cf: 4.826

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Pb ug/ml	final Cu ug/ml	final Pb ug/ml	init.Cu uM/l	init.Pb uM/l	final Cu uM/l	final Pb uM/l	Copper uptake uM	Copper soil up_take uM/g	Lead uptake uM	Lead soil up_take uM/g
1.990	1.805	4.580	0.190	0.530	0.014	0.006	2.990	2.558	0.222	0.030	0.138	0.077	0.126	0.070
2.030	1.841	4.580	0.420	1.200	0.021	0.011	6.610	5.791	0.331	0.051	0.314	0.171	0.287	0.156
2.000	1.814	4.600	0.620	1.330	0.018	0.010	9.758	6.419	0.282	0.049	0.474	0.261	0.318	0.176
2.000	1.814	4.580	0.810	2.400	0.019	0.011	12.748	11.582	0.301	0.052	0.622	0.343	0.577	0.318
2.010	1.823	4.560	1.020	2.670	0.026	0.018	16.053	12.885	0.401	0.085	0.783	0.429	0.640	0.351
1.990	1.805	4.620	1.241	3.600	0.027	0.020	19.531	17.374	0.427	0.095	0.955	0.529	0.864	0.479
1.990	1.805	4.560	1.390	4.130	0.030	0.023	21.876	19.931	0.474	0.109	1.070	0.593	0.991	0.549
1.990	1.805	4.760	1.600	4.800	0.032	0.022	25.181	23.165	0.499	0.108	1.234	0.684	1.153	0.639
2.000	1.814	4.540	1.830	5.330	0.034	0.028	28.801	25.723	0.540	0.135	1.413	0.779	1.279	0.705
1.990	1.805	4.600	2.010	6.000	0.039	0.035	31.634	28.956	0.609	0.171	1.551	0.859	1.439	0.797
1.990	1.805	4.540	7.720	20.400	0.147	0.377	121.498	98.451	2.314	1.819	5.959	3.302	4.832	2.677
2.010	1.823	4.420	13.710	40.000	0.291	0.432	215.770	193.041	4.580	2.085	10.559	5.792	9.548	5.237
2.000	1.814	4.460	19.880	60.000	1.075	1.300	312.874	289.561	16.918	6.274	14.798	8.158	14.164	7.808

coapetitive uptake: Cu vs Zn
soil: ahz
oven dry cf: 0.941 Cu cf: 15.738 Zn cf: 15.295

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Zn ug/ml	final Cu ug/ml	final Zn ug/ml	init.Cu uM/l	init.Zn uM/l	final Cu uM/l	final Zn uM/l	Copper uptake uM	Copper soil up_ take uM/g	Zinc uptake uM	Zinc soil up_ take uM/g
2.030	1.910	4.340	0.200	0.200	0.037	1.550	3.148	3.059	0.579	23.708	0.128	0.067	-1.032	-0.540
2.010	1.891	4.300	0.390	0.400	0.043	1.900	6.138	6.118	0.680	29.061	0.273	0.144	-1.147	-0.606
2.020	1.901	4.300	0.610	0.590	0.051	1.900	9.600	9.024	0.801	29.061	0.440	0.231	-1.002	-0.527
2.020	1.901	4.260	0.790	0.780	0.066	2.060	12.433	11.930	1.032	31.508	0.570	0.300	-0.979	-0.515
2.010	1.891	4.300	0.970	0.950	0.072	2.060	15.266	14.530	1.138	31.508	0.706	0.373	-0.849	-0.449
2.000	1.882	4.260	1.160	1.180	0.085	2.170	18.256	18.048	1.338	33.191	0.846	0.449	-0.757	-0.402
2.010	1.891	4.300	1.360	1.450	0.103	2.450	21.404	22.178	1.623	37.473	0.989	0.523	-0.765	-0.404
2.000	1.882	4.260	1.540	1.580	0.111	2.490	24.237	24.166	1.749	38.085	1.124	0.597	-0.696	-0.370
2.010	1.891	4.260	1.720	1.840	0.136	2.720	27.070	28.143	2.139	41.603	1.247	0.659	-0.673	-0.356
2.010	1.891	4.240	1.920	1.840	0.151	2.860	30.217	28.143	2.370	43.744	1.392	0.736	-0.780	-0.412
2.000	1.882	4.200	8.120	6.710	0.940	8.180	127.794	102.631	14.794	125.115	5.650	3.002	-1.124	-0.597
2.000	1.882	4.200	14.630	11.840	2.990	13.500	230.249	181.095	47.057	206.485	9.160	4.867	-1.270	-0.675
2.010	1.891	4.120	19.590	20.390	5.530	19.430	308.310	311.869	87.032	297.186	11.064	5.850	0.734	0.388

coapetitive uptake: Cu vs Zn
soil: fen arable
oven dry cf: 0.958 Cu cf: 15.738 Zn cf: 15.295

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Zn ug/ml	final Cu ug/ml	final Zn ug/ml	init.Cu uM/l	init.Zn uM/l	final Cu uM/l	final Zn uM/l	Copper uptake uM	Copper soil up_ take uM/g	Zinc uptake uM	Zinc soil up_ take uM/g
2.010	1.926	7.360	0.200	0.200	0.029	0.002	3.148	3.059	0.450	0.037	0.135	0.070	0.151	0.078
1.990	1.906	7.440	0.390	0.400	0.039	0.014	6.138	6.118	0.607	0.212	0.277	0.145	0.295	0.155
2.000	1.916	7.440	0.610	0.590	0.042	0.018	9.600	9.024	0.667	0.271	0.447	0.233	0.438	0.228
2.060	1.973	7.420	0.790	0.780	0.048	0.095	12.433	11.930	0.754	1.458	0.584	0.296	0.524	0.265
1.990	1.906	7.360	0.970	0.950	0.057	0.096	15.266	14.530	0.895	1.464	0.719	0.377	0.653	0.343
2.000	1.916	7.380	1.160	1.180	0.062	0.090	18.256	18.048	0.982	1.377	0.864	0.451	0.834	0.435
2.000	1.916	7.320	1.360	1.450	0.070	0.090	21.404	22.178	1.102	1.377	1.015	0.530	1.040	0.543
2.000	1.916	7.360	1.540	1.580	0.074	0.080	24.237	24.166	1.168	1.224	1.153	0.602	1.147	0.599
1.990	1.906	7.420	1.720	1.840	0.082	0.100	27.070	28.143	1.284	1.530	1.289	0.676	1.331	0.698
2.010	1.926	7.320	1.920	1.840	0.094	0.090	30.217	28.143	1.486	1.377	1.437	0.746	1.338	0.695
1.990	1.906	7.260	8.120	6.710	0.200	0.100	127.794	102.631	3.148	1.530	6.232	3.269	5.055	2.652
2.000	1.916	7.080	14.630	11.840	0.340	0.350	230.249	181.095	5.351	5.353	11.245	5.869	8.787	4.586
2.000	1.916	6.960	19.590	20.390	0.490	0.760	308.310	311.869	7.712	11.624	15.030	7.844	15.012	7.835

coapetitive uptake: Cu vs Zn
soil: arkleston
oven dry cf: 0.907 Cu cf: 15.738 Zn cf: 15.295

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Zn ug/ml	final Cu ug/ml	final Zn ug/ml	init.Cu uM/l	init.Zn uM/l	final Cu uM/l	final Zn uM/l	Copper uptake uM	Copper soil up_ take uM/g	Zinc uptake uM	Zinc soil up_ take uM/g
1.990	1.805	4.640	0.200	0.200	0.016	0.210	3.148	3.059	0.253	3.212	0.145	0.080	-0.008	-0.004
2.000	1.814	4.540	0.390	0.400	0.018	0.240	6.138	6.118	0.288	3.671	0.292	0.161	0.122	0.067
2.000	1.814	4.620	0.610	0.590	0.019	0.290	9.600	9.024	0.297	4.436	0.465	0.256	0.229	0.126
2.000	1.814	4.600	0.790	0.780	0.022	0.330	12.433	11.930	0.353	5.047	0.604	0.333	0.344	0.190
2.010	1.823	4.600	0.970	0.950	0.025	0.390	15.266	14.530	0.400	5.965	0.743	0.408	0.428	0.235
2.000	1.814	4.480	1.160	1.180	0.029	0.460	18.256	18.048	0.453	7.036	0.890	0.491	0.551	0.304
2.010	1.823	4.480	1.360	1.450	0.036	0.510	21.404	22.178	0.562	7.801	1.042	0.572	0.719	0.394
1.990	1.805	4.580	1.540	1.580	0.035	0.560	24.237	24.166	0.548	8.565	1.184	0.656	0.780	0.432
2.000	1.814	4.540	1.720	1.840	0.039	0.630	27.070	28.143	0.609	9.636	1.323	0.729	0.925	0.510
2.040	1.850	4.500	1.920	1.840	0.043	0.700	30.217	28.143	0.670	10.707	1.477	0.798	0.872	0.471
2.000	1.814	4.480	8.120	6.710	0.130	2.950	127.794	102.631	2.046	45.121	6.287	3.466	2.875	1.585
2.000	1.814	4.400	14.630	11.840	0.410	6.390	230.249	181.095	6.453	97.736	11.190	6.169	4.168	2.298
2.000	1.814	4.420	19.590	20.390	1.030	12.750	308.310	311.869	16.210	195.014	14.605	8.051	5.843	3.221

competitive uptake: Cu vs Cd,Fe,Pb,and Zn.
soil: ahz
oven dry cf: 0.941 Cu cf: 15.738 Cd cf: 8.897

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Cd ug/ml	final Cu ug/ml	final Cd ug/ml	init.Cu uM/l	init.Cd uM/l	final Cu uM/l	final Cd uM/l	Copper uptake uM	Copper soil up_ take uM/g	Cadmium uptake uM	Cadmium soil up take uM/
2.020	1.901	4.380	0.200	0.350	0.034	0.140	3.148	3.114	0.541	1.246	0.130	0.069	0.093	0.04
2.070	1.948	4.360	0.400	0.680	0.046	0.270	6.295	6.050	0.722	2.402	0.279	0.143	0.182	0.09
2.030	1.910	4.300	0.600	1.010	0.060	0.440	9.443	8.986	0.940	3.915	0.425	0.223	0.254	0.13
2.000	1.882	4.320	0.800	1.300	0.073	0.590	12.590	11.566	1.149	5.249	0.572	0.304	0.316	0.16
2.000	1.882	4.320	1.010	1.610	0.087	0.770	15.895	14.324	1.374	6.851	0.726	0.386	0.374	0.19
1.990	1.873	4.300	1.210	2.160	0.111	0.950	19.043	19.217	1.745	8.452	0.865	0.462	0.538	0.28
2.010	1.891	4.300	1.390	2.470	0.128	1.100	21.876	21.975	2.010	9.786	0.993	0.525	0.609	0.32
1.990	1.873	4.300	1.590	2.820	0.146	1.260	25.024	25.089	2.304	11.210	1.136	0.607	0.694	0.37
2.010	1.891	4.240	1.770	3.470	0.177	1.470	27.856	30.872	2.782	13.078	1.254	0.663	0.890	0.47
2.010	1.891	4.280	1.960	3.470	0.198	1.620	30.847	30.872	3.110	14.413	1.387	0.733	0.823	0.43
2.000	1.882	4.260	6.830	11.780	1.701	7.960	107.491	104.804	26.764	70.819	4.036	2.145	1.699	0.90
2.000	1.882	3.920	14.450	27.480	5.928	19.370	227.416	244.484	93.296	172.331	6.706	3.563	3.608	1.91
2.010	1.891	3.760	20.060	38.660	11.677	29.180	315.707	343.950	183.774	259.609	6.597	3.488	4.217	2.23

competitive uptake: Cu vs Cd,Fe,Pb,and Zn.
soil: fen arable
oven dry cf: 0.958 Cu cf: 15.738 Cd cf: 8.897

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Cd ug/ml	final Cu ug/ml	final Cd ug/ml	init.Cu uM/l	init.Cd uM/l	final Cu uM/l	final Cd uM/l	Copper uptake uM	Copper soil up_ take uM/g	Cadmium uptake uM	Cadmium soil up take uM/
1.990	1.906	7.080	0.200	0.350	0.034	0.003	3.148	3.114	0.535	0.026	0.131	0.069	0.154	0.08
2.020	1.935	7.120	0.400	0.680	0.035	0.010	6.295	6.050	0.556	0.086	0.287	0.148	0.298	0.15
1.990	1.906	7.120	0.600	1.010	0.046	0.010	9.443	8.986	0.727	0.086	0.436	0.229	0.445	0.23
1.990	1.906	7.000	0.800	1.300	0.052	0.015	12.590	11.566	0.820	0.132	0.589	0.309	0.572	0.30
2.000	1.916	6.980	1.010	1.610	0.060	0.018	15.895	14.324	0.941	0.161	0.748	0.390	0.708	0.37
1.990	1.906	7.120	1.210	2.160	0.060	0.022	19.043	19.217	0.943	0.197	0.905	0.475	0.951	0.49
2.000	1.916	7.120	1.390	2.470	0.069	0.025	21.876	21.975	1.091	0.222	1.039	0.542	1.088	0.56
2.000	1.916	7.080	1.590	2.820	0.073	0.030	25.024	25.089	1.149	0.268	1.194	0.623	1.241	0.64
2.000	1.916	6.860	1.770	3.470	0.085	0.038	27.856	30.872	1.342	0.337	1.326	0.692	1.527	0.79
1.990	1.906	7.120	1.960	3.470	0.083	0.035	30.847	30.872	1.308	0.312	1.477	0.775	1.528	0.80
2.010	1.926	6.840	6.830	11.780	0.207	0.254	107.491	104.804	3.263	2.258	5.211	2.706	5.127	2.66
1.990	1.906	6.080	14.450	27.480	0.299	0.978	227.416	244.484	4.703	8.703	11.136	5.841	11.789	6.18
2.000	1.916	5.520	20.060	38.660	0.421	2.585	315.707	343.950	6.621	23.000	15.454	8.066	16.048	8.37

competitive uptake: Cu vs Cd,Fe,Pb,and Zn.
soil: arkleston
oven dry cf: 0.907 Cu cf: 15.738 Cd cf: 8.897

soil wt. air (g)	soil wt. oven(g)	super pH	init. Cu ug/ml	init.Cd ug/ml	final Cu ug/ml	final Cd ug/ml	init.Cu uM/l	init.Cd uM/l	final Cu uM/l	final Cd uM/l	Copper uptake uM	Copper soil up_ take uM/g	Cadmium uptake uM	Cadmium soil up_ take uM/g
2.000	1.814	4.540	0.200	0.350	0.019	0.040	3.148	3.114	0.293	0.356	0.143	0.079	0.138	0.076
1.990	1.805	4.620	0.400	0.680	0.019	0.070	6.295	6.050	0.302	0.623	0.300	0.166	0.271	0.150
2.000	1.814	4.620	0.600	1.010	0.022	0.120	9.443	8.986	0.340	1.068	0.455	0.251	0.396	0.218
2.030	1.841	4.560	0.800	1.300	0.024	0.140	12.590	11.566	0.370	1.246	0.611	0.332	0.516	0.280
2.010	1.823	4.480	1.010	1.610	0.029	0.230	15.895	14.324	0.460	2.046	0.772	0.423	0.614	0.337
2.000	1.814	4.560	1.210	2.160	0.034	0.300	19.043	19.217	0.530	2.669	0.926	0.510	0.827	0.456
1.990	1.805	4.580	1.390	2.470	0.039	0.350	21.876	21.975	0.612	3.114	1.063	0.589	0.943	0.522
2.020	1.832	4.560	1.590	2.820	0.041	0.430	25.024	25.089	0.647	3.826	1.219	0.665	1.063	0.580
1.990	1.805	4.500	1.770	3.470	0.044	0.500	27.856	30.872	0.688	4.448	1.358	0.753	1.321	0.732
1.990	1.805	4.540	1.960	3.470	0.048	0.570	30.847	30.872	0.759	5.071	1.504	0.833	1.290	0.715
2.020	1.832	4.340	6.830	11.780	0.250	3.940	107.491	104.804	3.935	35.053	5.178	2.826	3.488	1.904
2.010	1.823	4.180	14.450	27.480	1.333	12.120	227.416	244.484	20.979	107.829	10.322	5.662	6.833	3.748
2.000	1.814	4.040	20.060	38.660	3.889	21.510	315.707	343.950	61.206	191.370	12.725	7.015	7.629	4.206

Appendix 4: Anion Type and Concentration Influence on Sorption: Cadmium and Copper.

effect of anion on Cd uptake
soil: arkleston
r1_r6:Citrate. r7_r12:Sulphate. r13_r18:Chloride.
soil cf: 0.91Cd cf: 8.897

soil wt. air	soil wt. oven	super pH	init. Cd ug/ml	final Cd ug/ml	init. Cd uM	final Cd uM	uptake uM	soil upt. uM/g
2.00	1.81	7.14	1.400	1.320	12.456	11.744	0.036	0.020
1.99	1.80	7.12	2.800	2.580	24.911	22.954	0.098	0.054
2.00	1.81	7.18	4.390	3.630	39.057	32.295	0.338	0.186
2.00	1.81	7.14	5.880	4.830	52.313	42.972	0.467	0.257
2.02	1.83	7.12	7.460	6.360	66.370	56.584	0.489	0.267
2.01	1.82	7.10	8.660	7.390	77.046	65.747	0.565	0.310
2.00	1.81	4.86	0.660	0.080	5.872	0.712	0.258	0.142
1.99	1.80	4.82	1.280	0.160	11.388	1.423	0.498	0.276
2.01	1.82	4.76	2.200	0.240	19.573	2.135	0.872	0.478
2.04	1.85	4.74	2.800	0.320	24.911	2.847	1.103	0.596
1.99	1.80	4.72	3.400	0.400	30.249	3.559	1.335	0.739
2.04	1.85	5.14	4.200	0.400	37.367	3.559	1.690	0.914
1.99	1.80	4.82	0.630	0.190	5.605	1.690	0.196	0.108
1.99	1.80	4.82	1.230	0.390	10.943	3.470	0.374	0.207
1.99	1.80	4.82	2.020	0.580	17.972	5.160	0.641	0.355
1.99	1.80	4.88	2.700	0.840	24.021	7.473	0.827	0.458
2.00	1.81	4.88	3.260	1.060	29.004	9.431	0.979	0.539
2.00	1.81	4.84	3.910	1.250	34.786	11.121	1.183	0.652

effect of anion on Cd uptake
soil: ahz
r1_r6:Citrate. r7_r12:Sulphate. r13_r18:Chloride.
soil cf: 0.94Cd cf: 8.897

soil wt. air	soil wt. oven	super pH	init. Cd ug/ml	final Cd ug/ml	init. Cd uM	final Cd uM	uptake uM	soil upt. uM/g
2.00	1.88	7.06	1.400	1.610	12.456	14.324	-0.093	-0.050
2.00	1.88	7.04	2.800	2.710	24.911	24.110	0.040	0.021
2.01	1.89	7.08	4.390	4.370	39.057	38.879	0.009	0.005
1.99	1.87	7.02	5.880	6.070	52.313	54.004	-0.085	-0.045
1.99	1.87	7.04	7.460	6.900	66.370	61.388	0.249	0.133
2.00	1.88	7.04	8.660	7.630	77.046	67.883	0.458	0.243
2.00	1.88	4.68	0.660	0.260	5.872	2.313	0.178	0.095
2.00	1.88	4.58	1.280	0.500	11.388	4.448	0.347	0.184
2.00	1.88	4.56	2.200	0.760	19.573	6.762	0.641	0.340
2.04	1.92	4.58	2.800	1.020	24.911	9.075	0.792	0.412
2.00	1.88	4.50	3.400	1.360	30.249	12.100	0.907	0.482
1.99	1.87	4.48	4.200	1.880	37.367	16.726	1.032	0.551
2.03	1.91	4.46	0.630	0.460	5.605	4.093	0.076	0.040
2.00	1.88	4.44	1.230	0.880	10.943	7.829	0.156	0.083
2.00	1.88	4.48	2.020	1.280	17.972	11.388	0.329	0.175
2.00	1.88	4.50	2.700	1.720	24.021	15.302	0.436	0.232
2.00	1.88	4.48	3.260	2.400	29.004	21.352	0.383	0.203
2.03	1.91	4.48	3.910	2.880	34.786	25.623	0.458	0.240

effect of anion on Cd uptake
soil: fen arable
r1_r6:Citrate. r7_r12:Sulphate. r13_r18:Chloride.
soil cf: 0.96Cd cf: 8.897

soil wt. air	soil wt. oven	super pH	init. Cd ug/ml	final Cd ug/ml	init. Cd uM	final Cd uM	uptake uM	soil upt. uM/g
2.00	1.92	7.80	1.400	0.210	12.456	1.868	0.529	0.276
2.01	1.93	7.76	2.800	0.430	24.911	3.826	1.054	0.548
2.00	1.92	7.78	4.390	0.660	39.057	5.872	1.659	0.866
2.01	1.93	7.74	5.880	0.840	52.313	7.473	2.242	1.164
2.00	1.92	7.78	7.460	1.080	66.370	9.609	2.838	1.481
1.99	1.91	7.74	8.660	1.210	77.046	10.765	3.314	1.738
1.99	1.91	7.28	0.660	0.020	5.872	0.178	0.285	0.149
1.99	1.91	7.32	1.280	0.030	11.388	0.267	0.556	0.292
2.01	1.93	7.38	2.200	0.040	19.573	0.356	0.961	0.499
1.99	1.91	7.28	2.800	0.050	24.911	0.445	1.223	0.642
2.00	1.92	7.26	3.400	0.060	30.249	0.534	1.486	0.775
1.99	1.91	9.12	4.200	0.070	37.367	0.623	1.837	0.964
2.00	1.92	7.32	0.630	0.020	5.605	0.178	0.271	0.142
2.00	1.92	7.30	1.230	0.030	10.943	0.267	0.534	0.279
2.03	1.94	7.32	2.020	0.050	17.972	0.445	0.876	0.451
2.00	1.92	7.40	2.700	0.070	24.021	0.623	1.170	0.611
2.02	1.94	7.34	3.260	0.090	29.004	0.801	1.410	0.729
2.00	1.92	7.36	3.910	0.110	34.786	0.979	1.690	0.882

effect of anion on Cu uptake.
soil: arkleston
r1_r6:Citrate. r7_r12:Sulphate. r13_r18:Chloride.
soil cf: 0.91Cu cf: 15.736

soil wt. air	soil wt. oven	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uM	soil upt. uM/g
2.00	1.81	7.14	0.340	0.480	5.350	7.553	-0.110	-0.061
2.01	1.82	7.12	0.660	0.690	10.386	10.858	-0.024	-0.013
2.00	1.81	7.12	1.000	0.940	15.736	14.792	0.047	0.026
2.01	1.82	7.08	1.330	1.190	20.928	18.725	0.110	0.060
2.00	1.81	7.06	1.630	1.430	25.649	22.502	0.157	0.087
1.99	1.80	7.06	1.970	1.660	30.999	26.121	0.244	0.135
1.99	1.80	4.92	0.290	0.024	4.563	0.379	0.209	0.116
1.99	1.80	4.82	0.590	0.033	9.284	0.516	0.438	0.243
2.00	1.81	4.78	0.900	0.039	14.162	0.620	0.677	0.373
2.01	1.82	4.82	1.200	0.047	18.883	0.740	0.907	0.498
1.99	1.80	4.84	1.510	0.052	23.761	0.810	1.148	0.636
1.99	1.80	4.78	1.800	0.059	28.324	0.927	1.370	0.759
2.00	1.81	4.78	0.300	0.011	4.721	0.173	0.227	0.125
2.00	1.81	4.78	0.600	0.016	9.441	0.252	0.459	0.253
1.99	1.80	4.76	0.900	0.021	14.162	0.330	0.692	0.383
2.00	1.81	4.86	1.220	0.024	19.197	0.378	0.941	0.519
2.00	1.81	4.84	1.510	0.028	23.761	0.441	1.166	0.643
2.03	1.84	4.72	1.820	0.032	28.639	0.507	1.407	0.764

effect of anion on Cu uptake.
soil: ahz
r1_r6:Citrate. r7_r12:Sulphate. r13_r18:Chloride.
soil cf: 0.94Cu cf: 15.736

soil wt. air	soil wt. oven	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uM	soil upt. uM/g
1.99	1.87	7.08	0.340	1.360	5.350	21.400	-0.803	-0.429
2.00	1.88	7.04	0.660	1.650	10.386	25.964	-0.779	-0.414
2.00	1.88	7.04	1.000	1.890	15.736	29.740	-0.700	-0.372
2.02	1.90	7.04	1.330	2.160	20.928	33.989	-0.653	-0.344
1.99	1.87	7.04	1.630	2.430	25.649	38.238	-0.629	-0.336
1.99	1.87	7.04	1.970	2.720	30.999	42.801	-0.590	-0.315
2.00	1.88	4.68	0.290	0.060	4.563	0.944	0.181	0.096
2.02	1.90	4.54	0.590	0.070	9.284	1.101	0.409	0.215
1.99	1.87	4.62	0.900	0.100	14.162	1.574	0.629	0.336
2.03	1.91	4.58	1.200	0.100	18.883	1.574	0.865	0.453
2.02	1.90	4.58	1.510	0.110	23.761	1.731	1.101	0.579
2.02	1.90	4.58	1.800	0.140	28.324	2.203	1.306	0.687
2.01	1.89	4.40	0.300	0.034	4.721	0.532	0.209	0.111
1.99	1.87	4.42	0.600	0.053	9.441	0.837	0.430	0.230
2.02	1.90	4.46	0.900	0.079	14.162	1.245	0.646	0.340
2.00	1.88	4.48	1.220	0.097	19.197	1.525	0.884	0.470
2.00	1.88	4.42	1.510	0.121	23.761	1.901	1.093	0.581
2.02	1.90	4.44	1.820	0.155	28.639	2.433	1.310	0.689

effect of anion on Cu uptake.
soil: fen arable
r1_r6:Citrate. r7_r12:Sulphate. r13_r18:Chloride.
soil cf: 0.96Cu cf: 15.74

soil wt. air	soil wt. oven	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM	final Cu uM	uptake uM	soil upt. uM/g
2.01	1.93	8.24	0.34	0.22	5.35	3.46	0.09	0.05
2.01	1.93	7.88	0.66	0.34	10.39	5.35	0.25	0.13
2.00	1.92	7.78	1.00	0.42	15.74	6.61	0.46	0.24
2.00	1.92	7.80	1.33	0.53	20.93	8.34	0.63	0.33
2.00	1.92	7.74	1.63	0.62	25.65	9.76	0.79	0.41
2.00	1.92	7.80	1.97	0.71	31.00	11.17	0.99	0.52
1.99	1.91	7.30	0.29	0.05	4.56	0.79	0.19	0.10
2.00	1.92	7.30	0.59	0.07	9.28	1.10	0.41	0.21
2.00	1.92	7.38	0.90	0.08	14.16	1.26	0.65	0.34
1.99	1.91	7.28	1.20	0.10	18.88	1.57	0.87	0.45
2.01	1.93	7.18	1.51	0.12	23.76	1.89	1.09	0.57
1.99	1.91	7.04	1.80	0.14	28.32	2.20	1.31	0.69
2.00	1.92	7.28	0.30	0.02	4.72	0.39	0.22	0.11
2.00	1.92	7.42	0.60	0.03	9.44	0.48	0.45	0.23
2.00	1.92	7.32	0.90	0.04	14.16	0.59	0.68	0.35
2.02	1.94	7.32	1.22	0.05	19.20	0.73	0.92	0.48
2.00	1.92	7.36	1.51	0.05	23.76	0.85	1.15	0.60
2.00	1.92	7.36	1.82	0.06	28.64	0.95	1.38	0.72

effect of electrolyte concentration.

soil; arkleston

NaNO3 M; M/60_M/30soil cf; 0.907Cu cf; 15.736

soil wt. air	soil wt. oven	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM/l	final Cu uM/l	Cu upt. uM	Cu upt. uM/g
1.990	1.805	5.020	0.310	0.018	4.878	0.283	0.230	0.127
2.010	1.823	4.980	0.638	0.029	10.039	0.463	0.479	0.263
2.000	1.814	4.980	0.984	0.038	15.484	0.603	0.744	0.410
2.000	1.814	4.880	1.307	0.047	20.566	0.738	0.991	0.547
1.980	1.796	4.940	1.626	0.050	25.586	0.788	1.240	0.690
2.000	1.814	4.920	1.958	0.042	30.810	0.656	1.508	0.831
2.010	1.823	4.820	0.265	0.017	4.170	0.269	0.195	0.107
2.020	1.832	4.860	0.586	0.021	9.221	0.337	0.444	0.242
1.990	1.805	4.920	0.922	0.025	14.508	0.395	0.706	0.391
1.990	1.805	7.000	1.257	0.030	19.780	0.472	0.965	0.535
1.990	1.805	4.880	1.555	0.036	24.469	0.563	1.195	0.662
2.000	1.814	4.880	1.885	0.043	29.662	0.681	1.449	0.799

effect of electrolyte concentration.

soil; ahz

NaNO3 M; M/60_M/30soil cf; 0.941Cu cf; 15.736

soil wt. air	soil wt. oven	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM/l	final Cu uM/l	Cu upt. uM	Cu upt. uM/g
1.990	1.873	4.580	0.310	0.032	4.878	0.508	0.218	0.117
1.990	1.873	4.600	0.638	0.041	10.039	0.647	0.470	0.251
2.010	1.891	4.620	0.984	0.040	15.484	0.625	0.743	0.393
2.010	1.891	4.600	1.307	0.055	20.566	0.861	0.985	0.521
2.030	1.910	4.580	1.626	0.062	25.586	0.979	1.230	0.644
2.020	1.901	4.580	1.958	0.074	30.810	1.164	1.482	0.780
1.990	1.873	4.560	0.265	0.027	4.170	0.426	0.187	0.100
2.000	1.882	4.520	0.586	0.035	9.221	0.557	0.433	0.230
2.000	1.882	4.580	0.922	0.049	14.508	0.769	0.687	0.365
2.000	1.882	4.540	1.257	0.052	19.780	0.810	0.948	0.504
2.000	1.882	4.580	1.555	0.066	24.469	1.034	1.172	0.623
2.010	1.891	4.540	1.885	0.081	29.662	1.281	1.419	0.750

effect of electrolyte concentration.

soil; fen arable.

NaNO3 M; M/60_M/30soil cf; 0.958Cu cf; 15.736

soil wt. air	soil wt. oven	super pH	init.Cu ug/ml	final Cu ug/ml	init.Cu uM/l	final Cu uM/l	Cu upt. uM	Cu upt. uM/g
2.000	1.916	7.320	0.310	0.032	4.878	0.499	0.219	0.114
1.990	1.906	7.340	0.638	0.045	10.039	0.702	0.467	0.245
2.010	1.926	7.340	0.984	0.058	15.484	0.913	0.729	0.378
2.000	1.916	7.320	1.307	0.068	20.566	1.065	0.975	0.509
2.000	1.916	7.320	1.626	0.074	25.586	1.169	1.221	0.637
2.000	1.916	7.320	1.958	0.082	30.810	1.282	1.476	0.771
1.990	1.906	7.260	0.265	0.036	4.170	0.562	0.180	0.095
2.010	1.926	7.220	0.586	0.044	9.221	0.692	0.426	0.221
2.020	1.935	7.300	0.922	0.055	14.508	0.864	0.682	0.353
2.020	1.935	7.280	1.257	0.064	19.780	1.004	0.939	0.485
2.000	1.916	7.320	1.555	0.072	24.469	1.131	1.167	0.609
2.000	1.916	7.360	1.885	0.083	29.662	1.312	1.417	0.740

effect of electrolyte concentration.

soil; arkleston

NaNO3 M; M/60_M/30soil cf; 0.907Cd cf; 8.897

soil wt. air	soil wt. oven	super	pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM/l	final Cd uM/l	Cd upt. uM	Cd upt. uM/g
2.010	1.823	5.020		0.480	0.034	4.270	0.302	0.198	0.109
2.000	1.814	5.020		1.080	0.047	9.609	0.418	0.460	0.253
2.000	1.814	5.040		1.600	0.071	14.235	0.632	0.680	0.375
2.010	1.823	5.120		2.200	0.100	19.573	0.890	0.934	0.512
2.030	1.841	4.940		2.800	0.135	24.911	1.201	1.185	0.644
2.000	1.814	5.020		3.200	0.171	28.470	1.521	1.347	0.743
2.000	1.814	4.980		0.520	0.031	4.626	0.276	0.218	0.120
2.000	1.814	4.980		1.100	0.070	9.786	0.623	0.458	0.253
2.010	1.823	4.980		1.600	0.107	14.235	0.952	0.664	0.364
2.000	1.814	4.920		2.200	0.152	19.573	1.352	0.911	0.502
2.000	1.814	4.920		2.800	0.193	24.911	1.717	1.160	0.639
2.000	1.814	4.920		3.400	0.234	30.249	2.082	1.408	0.776

effect of electrolyte concentration.

soil; ahz

NaNO3 M; M/60_M/30soil cf; 0.941Cd cf; 8.897

soil wt. air	soil wt. oven	super	pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM/l	final Cd uM/l	Cd upt. uM	Cd upt. uM/g
1.990	1.873	4.600		0.480	0.094	4.270	0.836	0.172	0.092
2.000	1.882	4.620		1.080	0.184	9.609	1.637	0.399	0.212
2.000	1.882	4.640		1.600	0.278	14.235	2.473	0.588	0.312
2.030	1.910	4.600		2.200	0.387	19.573	3.443	0.806	0.422
2.000	1.882	4.620		2.800	0.505	24.911	4.493	1.021	0.542
2.000	1.882	4.580		3.200	0.622	28.470	5.534	1.147	0.609
2.020	1.901	4.460		0.520	0.129	4.626	1.148	0.174	0.092
1.990	1.873	4.560		1.100	0.279	9.786	2.482	0.365	0.195
1.990	1.873	4.560		1.600	0.429	14.235	3.817	0.521	0.278
2.000	1.882	4.580		2.200	0.593	19.573	5.276	0.715	0.380
2.000	1.882	4.580		2.800	0.724	24.911	6.441	0.923	0.491
2.010	1.891	4.520		3.400	0.868	30.249	7.722	1.126	0.595

effect of electrolyte concentration.

soil; fen arable.

NaNO3 M; M/60_M/30soil cf; 0.958Cd cf; 8.897

soil wt. air	soil wt. oven	super	pH	init.Cd ug/ml	final Cd ug/ml	init.Cd uM/l	final Cd uM/l	Cd upt. uM	Cd upt. uM/g
2.000	1.916	7.320		0.480	0.019	4.270	0.169	0.205	0.107
2.010	1.926	7.340		1.080	0.010	9.609	0.087	0.476	0.247
1.990	1.906	7.340		1.600	0.010	14.235	0.085	0.707	0.371
2.000	1.916	7.360		2.200	0.012	19.573	0.107	0.973	0.508
2.000	1.916	7.340		2.800	0.016	24.911	0.140	1.239	0.646
2.000	1.916	7.300		3.200	0.019	28.470	0.168	1.415	0.739
2.000	1.916	7.320		0.520	0.007	4.626	0.062	0.228	0.119
2.000	1.916	7.320		1.100	0.010	9.786	0.092	0.485	0.253
2.020	1.935	7.320		1.600	0.014	14.235	0.125	0.706	0.365
2.010	1.926	7.380		2.200	0.017	19.573	0.149	0.971	0.504
2.000	1.916	7.380		2.800	0.020	24.911	0.179	1.237	0.645
2.020	1.935	7.360		3.400	0.027	30.249	0.245	1.500	0.775

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